

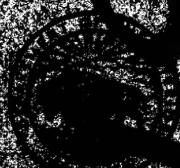
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A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks

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A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks

By H. W. FAIRBAIRN and others

CONTRIBUTIONS TO GEOCHEMISTRY, 1950-51

GEOLOGICAL SURVEY BULLETIN 980

*An investigation by staff members of
Department of Geology, Massachusetts
Institute of Technology, Cambridge,
Mass. (in collaboration with Office of Contract No.
Naval Research, Washington, D. C.); N5or1-07830
Geophysical Laboratory, Carnegie In-
stitution of Washington, Washington,
D. C.; Geochemistry and Petrology
Branch, U. S. Geological Survey,
Washington, D. C.*



UNITED STATES DEPARTMENT OF THE INTERIOR

Oscar L. Chapman, *Secretary*

GEOLOGICAL SURVEY

W. E. Wrather, *Director*

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CONTRIBUTIONS TO GEOCHEMISTRY, 1950-51

FOREWORD

BY EARL INGERSON

This bulletin is the second of the series "Contributions to Geochemistry" which was begun in 1946 with Bulletin 950, "Contributions to Geochemistry, 1942-45". This series is the successor to earlier ones, also published as U. S. Geological Survey Bulletins, "Report of work done in the Division of Chemistry and Physics" (1879-1893), "Contributions to chemistry and mineralogy from the laboratory of the United States Geological Survey" (1900), "Contributions to mineralogy from the United States Geological Survey" (1905), and "Mineralogical Notes" (1911-16). A third member of the current series is essentially ready for publication and we hope still others will appear from time to time.

"Contributions to Geochemistry, 1942-45" consisted entirely of reports of work done by Survey staff members, as did most of the earlier series mentioned above. Much of the noteworthy progress in the earth sciences is being made possible by the cooperation of scientists in different disciplines and in various institutions. It is particularly gratifying, therefore, to present in this bulletin a report of cooperative work with geochemical laboratories throughout the world, studied, interpreted, and prepared for publication by spectrographers, geochemists, and petrologists. The results will give an insight into the current status of spectrographic and chemical analysis of silicate rocks that could not have been obtained by any amount of work by one group of scientists working in one laboratory.

It is a pleasure to express, on behalf of the staff members of the Branch of Geochemistry and Petrology, our sincere thanks to the many scientists who, at considerable sacrifice of their special interests, participated so generously and conscientiously in this project. I also wish to express our appreciation to the other cooperating institutions, the Massachusetts Institute of Technology and the Geophysical Laboratory of the Carnegie Institution of Washington.

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A COOPERATIVE INVESTIGATION OF
PRECISION AND ACCURACY IN
CHEMICAL, SPECTROCHEMICAL, AND MODAL ANALYSIS OF
SILICATE ROCKS

PART 1. PREPARATION AND DISTRIBUTION OF THE
SAMPLES

BY H. W. FAIRBAIRN ¹

Whosoever shall entertain high and vaporous imaginations, instead of a laborious and sober inquiry of truth, shall beget hopes and beliefs of strange and impossible shapes.

—*Francis Bacon.*

The eminent Elizabethan author of the above lines doubtless had in mind a much broader horizon for his "sober inquiry of truth" than the limited level of inquiry which we will pursue in the pages to follow. Nevertheless his pronouncement is entirely apposite, whatever the scale, and characterizes in a single phrase the nature of the investigation we are presenting here. This investigation, in its present form, is concerned with the fundamental matter of precision and accuracy as applied to chemical, spectrochemical, and modal analyses of rocks. Despite the dependence of petrologists and geochemists on such analyses, there has been little attempt at critical evaluation of the procedures used. We are presenting in this bulletin some facts and ideas which may stimulate interest in this aspect of quantitative measurement.

Although the investigation as presented here is the work of many people, it had its immediate roots some 2 years ago in the Geology Department of the Massachusetts Institute of Technology as part of a program of spectrographic research under H. W. Fairbairn, supervisor, and L. H. Ahrens, associate supervisor, and sponsored by the Office of Naval Research, Washington, D. C. It was agreed at that time that the spectrograph might play a very useful role in quantitative work on the major elements of rocks, a role heretofore reserved for the minor elements. This minor-element role is in part a result of expediency, since chemists could not on the whole do satisfactory work with the low concentrations of the minor elements, whereas the field

¹ Massachusetts Institute of Technology.

of the major elements was tacitly recognized as their preserve. Since progress always involves intrusion into new ground, it was decided to reconnoiter this new field² of spectroscopy of the major elements, not with the idea of supplanting the chemists' work, but rather with the object of utilizing the economies in time and expense offered by the spectrograph. Chemical analyses of silicate rocks are at best expensive, if one has the work done by a reputable analyst, or are time-consuming if one has the skill and courage to make one's own. It is therefore tempting to pit the possibilities of the spectrograph against the unavoidable disadvantages of time and expense which handicap the chemist in his role as geological aide.

Work in the Cabot Spectrographic Laboratory at Massachusetts Institute of Technology established the feasibility of quantitative analyses of most of the major elements: the analysis requires only a few hours to complete, and gives a precision—reproducibility—of about 5 percent. (See part 3 of this report.) Obviously the next step was to obtain a measure of the accuracy—degree of approach to the absolute value—of the determinations made. One way was to prepare synthetic standards, in which the tolerances of each constituent would be known, and so provide a reference level for spectrographic determination of unknowns of the major elements. A second way was to prepare a provisional standard sample of a natural rock and have replicate chemical analyses made, the average value for each constituent to serve as control for the spectrographic determination. The matter was decided in favor of the second method (part 3 of this report), as it was believed that lack of a natural rock matrix in a synthetic standard might lead to errors difficult or impossible to evaluate. There was the additional advantage that a large stock of the natural rock could be made up as a standard and be available for calibration over a long period of time. On the other hand, the synthesis of a comparable rock in large quantities would be an impracticable task.

Two factors entered into the selection of a natural rock standard: It seemed advisable to use a silicate rock of widespread occurrence, and there would be an advantage in using a massive, medium-grained homogeneous material so that statistical analysis of the mode could be undertaken. These demands could be met, for example, in many types of granite and diabase. By a fortunate coincidence we learned that Dr. Felix Chayes, of the Geophysical Laboratory, had already selected a granite from Westerly, Rhode Island, for modal analysis. We immediately joined forces with him and decided to use this rock for calibration purposes, since any chemical data we might obtain

² Reference to previous and contemporary work by other investigators will be found in Part 3 of this report, page 21.

would obviously be of immense interest for his modal analyses. He immediately took steps to obtain additional material and have it processed for chemical study. Dr. Chayes' report on the work follows.

The granite was purchased from the Smith Granite Co. of Westerly, R. I., and was quarried from their principal working as of June 1947. It was received as a single rough-finished strip with cross section about 6 inches by 6 inches and a little over 6 feet long. The strip was sand-blasted to remove dirt and paint. Eight slugs, approximately 4 inches by 2 inches by 2 inches were taken at 6-inch intervals along the strip. These were numbered consecutively, and a thin section was prepared from tablets sawed from each end of each slug in the plane of the hardway.

The remainder of the strip was broken into large pieces by sledge hammer, and these were passed through a 4-inch by 6-inch jaw crusher. The entire primary crusher product was then passed through a 2-inch by 3-inch jaw crusher and the product of this operation screened on a 10-mesh Hummer vibrating screen. Oversize from this operation was put through a rolls crusher with stage screening until the entire product was minus 10-mesh. The complete sample was then screened, by hand on an 80-mesh 8-inch sieve and the plus 80-mesh product ground in 2-pound batches in 8-inch Abbe mills with mullite balls. The grinding operation was performed in 15-minute passes, undersize material being removed by sieve between successive passes. A 50-gram grab sample of the original undersize from the rolls, a 50-gram sample of the finished pebble-mill product—also grab—and the slugs mentioned above are stored in my laboratory.

Of 106 pounds of granite available for the crushing, 96 pounds were recovered in -80-mesh material. Most of the loss was encountered in the jaw crushing. During this operation pebbles up to 3 inches in diameter, but mostly smaller, were frequently thrown out of the machine by the wedging action of the jaws. In order to reduce chances of contamination we decided at the outset to discard fragments lost in this fashion; most of the 10-pound loss could otherwise have been recovered. Using a hand lens I could detect no difference between fragments which popped out of the crushers and those that stayed in, and I do not believe the failure to retrieve them introduced any significant bias.

The size reduction just described was performed by W. E. Warnke, of the Bureau of Mines, at the Eastern Experiment Station of the Bureau, College Park, Md., and most of the preceding discussion is a paraphrase of his report. For permission to use the facilities of the College Park Station we are indebted to Frank Lamb.

The -80-mesh powder was then delivered to Mr. R. A. Heindl, of the National Bureau of Standards, who arranged for the final mixing of roll and pebble-mill products, as there were no proper facilities for this operation at College Park. The entire 96 pounds of powder was tumbled for 5 hours in a large porcelain-lined mill with a small load of carefully cleaned flint pebbles.

At about this time we learned, through Dr. Chayes, that a few years earlier, Dr. W. T. Schaller, of the United States Geological Survey, had prepared a diabase sample with the intention of using it for control purposes in chemical work on rocks. By mutual agreement with Dr. Michael Fleischer, at present in charge of this type of investigation at the Geological Survey, the Massachusetts Institute of Technology and Geophysical Laboratory groups joined with the

Federal Survey in an over-all spectrochemical-chemical-modal study based on both the granite and diabase standards. The powdered granite already prepared under the supervision of Dr. Chayes was turned over to W. G. Schlecht, of the Geological Survey, for bottling, distribution, and storage. Mr. Schlecht's report on this final aspect of the sampling is as follows:

The 96 pounds of powdered granite received from Felix Chayes was heaped on a large canvas and divided into two equal parts. Grab samples were taken from one of the halves, as follows: Four 70-gram grab samples, labeled G-1-S, were taken for spectrographic analysis, as well as two additional 1-pound grab samples, labeled G-1-A. These are being kept for comparison with the mixed sample, represented by G-1, in the event of suspicion that contamination was introduced during the mixing and bottling process. This half was again divided into two parts by quartering. One of these parts was split by passing through a Jones sample splitter, and the process was repeated until two 1-pound samples, labeled G-1-B, were left; these are being kept as representative of the batch, in case any evidence is found that either the unmixed sample, represented by G-1-A, or the mixed sample, represented by G-1, are inhomogeneous.

Each of the original two halves of the 96-pound lot was mixed by shoveling and by shifting on the canvas. The two halves were combined in the original container and transferred to 562 jars labeled G-1, containing about 76 grams each and totaling about 90 pounds of powder.

Complete information on the processing of the diabase is not available owing to the death of one of the persons concerned. Mr. Schlecht has furnished the following:

The diabase, of Triassic age, was collected December 6, 1946, by W. T. Schaller and Norman Davidson, at Bull Run Quarry, on U. S. Highway 211, 3¼ miles southwest of Centerville, Fairfax County, Va. Lumps of several pounds each, totaling 260 pounds, were picked from the quarry floor, taking care to avoid inclusions of secondary vein material.

About a dozen of the lumps were saved for hand specimens, thin sections, and other purposes. The rest was reduced to about 10-mesh in the Geological Survey shop and ground in a ball mill at the National Bureau of Standards until it passed a 100-mesh screen. The powdered rock was heaped on a canvas and divided into two parts by quartering. Each half was again divided by quartering and each of the four resulting portions was mixed by shoveling and by shifting on the canvas. The whole lot was combined in the original container and transferred to 1,382 jars labeled W-1, containing about 70 grams each and totalling about 210 pounds of powder.

The matter of contamination of the rock powders as a result of the processing is of no significance insofar as the material is used as a standard and is thoroughly mixed. Where the analytical results are to be used as a measure of the original composition of the rock, however, it must be remembered that alumina, silica, and iron may have entered the sample in appreciable amounts because of the abrasion of the rolls and containers. There is no practical way of removing any of this extraneous material—except possibly tramp iron—and

allowance must therefore be made for it in terms of original rock composition.

An indication that the mixing has been adequate and that the bottled samples are identical for practical purposes is shown by the low relative error for SiO_2 in the two rocks. (See pt. 3, table 14 for details.) The values obtained are very small relative to those for the other constituents.

It was realized that, whatever the outcome of the present investigation, possession of a large store of such standard samples would be of immense future value to analysts of all kinds as a means of both intralaboratory and interlaboratory control. The chemical results discussed in parts 2 and 3 of this report indicate that the time for such control is long overdue.

In order to obtain a broad coverage of chemical analyses it was decided to enlist the support of all types of laboratories—university, government, and commercial—in various parts of the world, and to request routine analysis of each prepared standard, in duplicate if possible. This task fell to the writer and all expense incurred was borne by the Office of Naval Research. The response to our request for cooperation was unanimous and within a year 24 laboratories had furnished us with over 30 analyses of each rock, almost half of them in duplicate. Most of the government laboratories made no charge for the work. To all participants, whether analysts or supervisors, goes our deep appreciation for their willing and prompt cooperation, without which we would have been greatly handicapped. A list of the contributing laboratories and of the analysts—as far as we know them—is given in part 2 (pp. 23–24).

The results of the chemical work turned out to be more interesting than was anticipated, but not in a way to solve completely the original spectrographic problem. In consequence part 2 and some of part 3 are devoted to their evaluation. The original purpose of providing accurate calibration for spectrochemical work on the major elements was not realized except for a few constituents, since the spectrographic precision turned out to be superior in many respects to that obtained by chemical means (pt. 3 of this report). Similarly, the precision obtained by modal analysis proved superior to that shown by norms calculated from the individual chemical analyses (parts 2 and 4). These comparisons are unfair in the sense that in each example an interlaboratory (chemical) result is contrasted with one of intralaboratory character only (spectrographic, modal). Nevertheless, the relatively enormous discrepancies in some of the chemical results, part 3 (figs. 1–3) bespeak more than normal variations and indicate an urgent need for thorough interlaboratory standardization.

An independent project on interlaboratory determination of minor elements in the two standard rocks has been supervised by Dr. Ahrens, with results to date shown in part 5. Although there is no easy way to eliminate systematic errors in minor-element determination, the results are distinctly encouraging. It is hoped that interlaboratory work on uranium and thorium will also be carried out.

No part of the project under discussion in the following chapters is in any sense complete. In terms of the Baconian slogan which heads this chapter, our "sober inquiry after truth" would definitely "beget hopes and beliefs of strange and impossible shapes" were we to state otherwise. Since problems dealing with precision and accuracy literally have no final solution one must be content with reports of progress. This bulletin is such a report of progress, published at this time because we believe the topics under discussion are of surpassing interest to petrologists and geochemists.

A COOPERATIVE INVESTIGATION OF
PRECISION AND ACCURACY IN
CHEMICAL, SPECTROCHEMICAL, AND MODAL ANALYSIS OF
SILICATE ROCKS

PART 2. RESULTS OF CHEMICAL ANALYSIS OF SAMPLES
OF GRANITE AND DIABASE

BY WILLIAM G. SCHLECHT AND ROLLIN E. STEVENS ³

This comparison of results reported by 34 chemists analyzing the same rocks is the first step in what is probably the most comprehensive study ever undertaken on rock analysis. Although the discrepancies in results may seem great, they are not surprising in view of previous experience with rock analysis (Larsen, 1938). The results show what variability may be expected when a rock sample is analyzed by a large number of laboratories. In the absence of knowledge of the actual composition of the rocks no very precise estimate can be made of the errors to be expected; the ranges of values give an idea of how large the discrepancies can be.

When compared with the precision of spectrographic procedures reported in part 3 of this report the precision of the chemical determinations may appear very low, but it should be noted that the estimates of spectrographic precision represent determinations made in a single laboratory, as contrasted with the chemical determinations made in 25 laboratories. In part 3, table 18, chemical determinations made within a single laboratory are compared with the spectrographic determinations.

The disparity in results is too great at this preliminary stage to justify the assignment of "correct" values for the composition of the samples. Before they can be used as absolute standards on which calibrations are based, further work will have to be done to locate and correct the sources of the discrepancies in analytical results. It is hoped that further interlaboratory work will result in improvement of analytical procedures and in a more accurate estimate of the actual composition of the two rock samples.

All 34 collaborators analyzed the granite sample (G-1), and 30 of them analyzed the diabase sample (W-1). Their reports are given in tables 1 and 2, in which each analyst is represented by a code number.

³ U. S. Geological Survey.

Reports of collaborators are designated by numbers (1-34) in boxheads!

CIPW norms

Quartz	29.34	27.78	29.28	27.90	27.18	29.40	27.84	28.20	25.08	20.58	26.64	30.42	30.30	26.04	20.46	23.94	27.24
Orthoclase	32.80	32.80	31.74	31.69	33.36	29.47	33.36	31.69	32.80	32.80	34.47	31.69	31.69	32.80	33.36	40.50	32.80
Albite	26.72	28.82	27.77	31.96	29.34	30.39	27.77	29.34	32.49	27.77	27.25	26.72	26.72	33.51	29.34	24.00	26.72
Anorthite	6.12	6.12	6.12	4.45	6.12	5.00	6.39	5.56	5.00	9.2	7.23	5.56	5.56	6.35	6.35	6.12	6.12
Dioptase																	
Hypersthene	1.69	2.02	1.86	1.40	1.79	2.02	2.18	73	1.69	1.69	2.04	1.53	1.66	2.58	1.79	1.63	1.89
Magnetite	1.39	.93	1.39	1.39	1.16	1.16	.93	2.09	1.39	1.16	1.86	1.16	1.16	2.09	.93	1.39	1.39
Hematite																	
Humate																	
Pyrite																	
Adam																	
Zircon																	
Water																	
Total	99.88	100.25	99.62	99.75	100.12	99.68	99.88	99.80	99.08	100.39	100.87	99.72	99.85	100.30	100.21	99.89	100.06
Classification:																	
Class, Order	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4	I 4
Range, Subrang	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 3	2, 2	2, 3	2, 3	1, 3	2, 3	2, 3	2, 3

Classification:
Class, Order-
Rang, Subrang

	118	119	120	21	22	23	24	125	26	127	28	29	30	131	132	33	234
SiO ₂	71.54	72.46	72.23	72.45	72.40	72.04	72.30	72.46	71.60	72.34	72.36	72.43	72.48	71.88	72.17	72.37	72.34
Al ₂ O ₃	15.96	14.08	14.82	14.13	15.40	14.50	14.13	14.42	14.59	14.31	13.96	14.04	14.31	13.66	14.03	14.30	14.34
FeO	1.32	1.04	1.98	1.82	1.82	1.77	1.92	1.72	1.74	1.91	1.86	1.77	1.91	1.66	1.81	1.95	1.68
MnO	0.52	0.42	0.43	0.38	0.19	0.43	0.32	0.36	0.35	0.30	0.45	0.23	0.22	0.42	0.42	0.48	0.37
CaO	1.04	1.025	1.02	1.03	1.03	1.02	1.37	1.40	1.90	1.25	1.30	1.49	1.45	1.03	1.02	0.05	0.02
Na ₂ O	1.34	1.30	1.35	1.31	1.51	1.42	1.37	1.40	1.90	1.25	1.30	1.49	1.45	1.22	1.24	1.35	1.52
K ₂ O	3.48	3.25	3.45	3.45	2.61	3.26	3.29	3.04	3.16	3.35	3.30	3.17	3.38	2.78	3.41	2.98	3.37
H ₂ O	4.14	5.74	5.34	6.23	3.85	5.48	5.37	5.86	5.74	5.49	5.46	5.42	5.54	5.62	5.30	5.51	5.47
P ₂ O ₅	0.38	0.40	0.33	0.42	1.02	1.11	1.52	1.10	0.08	0.05	0.06	0.04	0.04	0.01	0.01	0.05	0.06
TiO ₂	0.20	0.28	0.26	0.26	1.16	1.25	1.35	1.24	0.26	0.26	0.25	0.26	0.26	0.27	0.26	0.31	0.26
P ₂ O ₅	Tr.	1.11	1.10	1.12	1.41	0.06	1.10	0.08	0.20	0.08	0.27	0.16	0.03	0.03	0.04	0.04	0.12
S	0			0.02													
CO ₂				10													
BaO																	
SiO ₂																	
Li ₂ O																	
Cr ₂ O ₃																	
V ₂ O ₅																	
ZrO ₂																	
Total	99.93	99.71	100.23	100.59	99.88	99.71	99.87	100.02	99.80	99.75	99.82	99.76	100.12	99.69	100.00	99.79	99.96

CIPW norms

	118	119	120	21	22	23	24	125	26	127	28	29	30	131	132	33	234
Quartz...	29.58	28.32	29.16	24.84	39.66	28.50	28.80	28.74	20.82	29.04	29.40	30.18	28.44	30.54	27.12	30.18	28.20
Orthoclase	26.69	33.02	31.14	37.25	22.80	32.25	31.69	35.03	33.92	32.25	32.25	31.69	32.80	33.36	32.80	32.80	31.69
Anorthite	29.34	27.25	27.77	29.34	22.01	27.77	28.30	25.08	26.72	28.30	27.77	28.30	28.30	23.58	28.82	25.15	28.30
Albite	6.67	5.56	6.67	4.45	5.00	6.12	5.56	6.12	8.62	5.00	4.73	6.67	6.39	6.12	7.23	6.39	6.67
Dioctahed				1.57	1.42	1.76	1.83	1.49	1.46	1.53	1.76	1.86	1.16	1.40	1.68	1.50	1.82
Hypersthene	2.88	1.89	1.76	1.66	1.16	1.16	1.39	1.93	1.93	1.39	1.16	1.02	1.39	2.32	1.46	1.62	1.16
Monazite																	
Hemite																	
Ilmenite	0.46	0.61	0.61	0.61	0.30	0.61	0.61	0.61	0.61	0.46	0.46	0.46	0.46	0.46	0.91	0.61	0.46
Apatite					1.01	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Corundum	2.96	0.51	1.33		5.10	0.92	0.61	0.71	0.34	1.02	0.92	0.51	0.41	0.81	0.61	0.92	0.41
Zircon																	
Water	0.51	0.43	0.41	0.35	1.44	0.49	0.52	0.51	0.36	0.40	0.63	0.53	0.44	0.78	0.27	0.35	0.36
Total	99.79	99.76	100.35	100.57	99.90	99.92	99.65	100.16	99.78	99.73	99.75	99.58	100.13	99.37	99.88	99.92	99.41

Classification:
Class, Order
Rank, Subrang

1 Mean of two analyses. 2 Received too late for inclusion in calculations in Part 3. 3 Loss on ignition. 4 Sample dried at 100° C. 5 Spectrographic determination.
6 Corrected for sulfur (-0.02). 7 Corrected for sulfur (-0.01). 8 Also reported PbO, 0.004 (spectrographic determination).

[Reports of collaborators are designated by numbers (1-5, 7-24, 26-28, 31-34) in boxheads]

	1	2	3	4	5	7	8	19	110	111	12	13	14	115	116
SiO ₂	52.56	52.58	52.12	53.01	52.59	52.48	52.45	52.35	51.71	52.35	52.42	52.55	51.35	51.35	51.28
Al ₂ O ₃	13.91	14.91	15.07	15.09	14.99	15.13	15.19	15.13	15.34	14.99	15.37	15.35	13.70	14.57	16.32
Fe ₂ O ₃	2.28	1.78	1.44	9.92	1.08	1.35	1.35	3.46	4.00	1.31	1.31	1.31	2.64	2.00	.28
FeO	8.92	8.78	8.81	9.16	8.89	8.78	8.42	8.56	6.90	8.67	8.69	8.16	8.26	8.26	9.38
MnO	6.67	6.70	6.74	5.69	6.54	6.64	6.52	6.50	6.52	6.59	6.60	6.68	6.13	6.13	6.67
MgO	17.17	16.16	16.13	21.16	10.88	10.98	10.55	11.19	11.04	10.79	10.95	10.89	11.42	11.29	11.29
CaO	10.82	11.00	11.04	10.86	10.88	10.98	10.55	11.19	11.04	10.79	10.95	10.89	11.42	11.29	11.29
Na ₂ O	2.09	2.14	2.09	2.40	2.28	2.15	2.17	1.98	1.88	2.15	2.01	2.09	2.28	2.48	2.06
K ₂ O	.74	.68	.60	.66	.68	.71	.61	.60	.65	.82	.63	.68	1.17	.82	1.30
H ₂ O	1.12	1.16	1.13	1.15	1.13	1.18	.67	.62	.62	.62	.62	.62	.62	.62	.62
H ₂ O +	1.12	1.16	1.13	1.15	1.13	1.18	.67	.62	.62	.62	.62	.62	.62	.62	.62
CO ₂	1.12	1.16	1.13	1.15	1.13	1.18	.67	.62	.62	.62	.62	.62	.62	.62	.62
P ₂ O ₅	1.12	1.16	1.13	1.15	1.13	1.18	.67	.62	.62	.62	.62	.62	.62	.62	.62
SO ₂	.04						0	.12	.11	.18	.13	.13	.14	.10	0(7)
CO							0							0	
B ₂ O ₃	.06						.04								
SiO					.02		.09								
Li ₂ O					.03		.03								
Cr ₂ O ₃															
V ₂ O ₅															
Total	100.11	100.13	99.82	99.86	99.92	100.30	99.90	100.22	100.40	100.06	99.92	100.12	100.14	100.04	100.23
CIPW norms															
Quartz	4.74	3.60	4.56	3.72	2.88	3.84	4.20	4.02	6.66	4.50	4.02	3.69	2.82	1.32	
Orthoclase	3.89	3.84	3.34	3.89	4.45	3.84	3.34	3.34	3.89	5.00	3.34	3.89	7.23	5.00	7.78
Albite	17.82	18.34	16.77	20.44	18.65	18.34	18.34	16.77	16.24	17.82	16.77	17.82	20.96	17.82	31.14
Anorthite	26.41	28.91	30.58	28.36	28.63	29.47	30.02	31.14	32.25	28.36	31.41	30.30	23.35	26.13	31.14
Diopside	21.64	20.98	19.16	20.69	20.10	20.37	18.46	19.97	17.30	19.99	18.80	18.95	24.51	24.39	20.62
Hypersthene	19.15	19.98	20.84	18.47	20.50	19.52	19.65	19.67	16.24	15.35	20.68	20.64	16.07	15.30	15.06
Olivine															4.97
Magnetite	3.25	2.09	2.09	1.39	1.62	2.09	2.55	2.09	5.10	5.90	1.86	1.86	3.71	3.02	.46
Ilmenite	2.13	1.98	1.98	1.98	1.98	1.98	1.98	2.13	1.67	2.13	2.13	2.13	2.28	2.74	2.13
Apatite	.34	.34	.34	.34	.34	.34	.34	.34	.34	.67	.34	.34	.34	.34	
Water	.64	.44	.59	.56	.59	.96	.07	.84	.04	.44	.66	.62	.56	.80	.58
Total	100.01	100.55	100.25	99.84	99.95	100.50	99.55	100.32	100.33	100.06	100.01	100.15	100.26	100.09	100.36
Classification: Class, order, Range, Subrange	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4	III.5 4,4

	117	118	119	120	21	22	23	124	26	127	28	131	132	33	34
SiO ₂	52.31	52.66	52.61	52.32	52.43	52.21	52.42	52.45	52.09	52.28	52.49	52.20	52.51	52.22	52.25
Al ₂ O ₃	15.18	14.96	14.66	15.41	14.86	16.56	15.04	14.83	18.57	14.92	14.51	14.50	15.28	15.19	15.13
FeO	1.74	1.08	1.32	1.22	1.57	4.26	1.43	1.13	1.33	3.80	1.19	1.45	1.51	1.92	1.92
Fe ₂ O ₃	8.55	9.22	8.80	9.12	8.67	6.80	8.80	8.95	8.81	7.02	8.98	9.07	8.57	8.68	8.02
MgO	6.79	7.09	6.66	6.76	6.70	5.49	7.09	6.26	4.27	6.22	6.20	6.16	6.57	6.40	6.74
MnO	11.18	10.26	10.37	10.32	10.57	11.72	11.04	10.80	10.64	10.92	10.90	11.02	10.81	11.07	10.98
CaO	2.60	1.91	1.88	2.03	2.62	1.61	1.94	1.78	1.98	1.98	2.18	1.75	2.09	1.82	2.11
Na ₂ O	2.60	1.91	1.88	2.03	2.62	1.61	1.94	1.78	1.98	1.98	2.18	1.75	2.09	1.82	2.11
K ₂ O	1.16	1.13	1.23	1.03	1.16	1.09	1.18	1.08	1.23	1.53	1.66	1.57	1.74	1.60	1.60
H ₂ O ⁺	1.16	1.13	1.23	1.03	1.16	1.09	1.18	1.08	1.23	1.53	1.66	1.57	1.74	1.60	1.60
H ₂ O ⁻	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13
TiO ₂	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13
P ₂ O ₅	1.15	1.08	1.16	1.12	1.03	1.08	1.13	1.10	1.15	1.16	1.17	1.18	1.06	1.09	1.03
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
BaO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Li ₂ O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cr ₂ O ₃	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
V ₂ O ₅	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	100.64	100.02	99.89	100.28	100.62	100.79	100.62	99.90	100.22	100.21	100.06	100.16	100.01	99.77	99.94

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CIPW norms

Quartz	3.36	4.68	3.96	3.66	1.50	8.82	4.14	5.22	3.96	6.90	3.54	5.64	4.62	5.10	3.36
Albite	3.34	2.22	5.90	3.34	3.89	3.89	3.34	3.34	4.45	3.34	3.89	3.34	2.78	3.89	3.34
Anorthite	18.34	16.24	16.77	16.77	22.01	13.62	16.24	15.20	16.77	16.77	18.34	16.20	17.82	15.20	17.82
Diorite	30.02	30.86	28.63	31.41	26.97	36.14	30.58	30.58	39.48	30.02	27.80	29.75	30.86	31.41	30.02
Hypersilene	20.03	17.59	20.31	18.27	21.64	14.68	19.13	18.46	10.51	18.88	21.02	19.52	17.99	18.06	21.93
Olivine	19.85	24.09	20.31	22.16	18.85	14.88	21.77	21.96	21.81	15.68	20.21	20.21	20.54	20.01	18.77
Magnetite	2.55	1.62	1.86	1.86	2.32	6.26	2.09	1.62	1.86	3.57	1.86	2.09	2.09	2.78	1.39
Ilmenite	2.13	1.67	2.13	1.98	2.13	1.96	2.13	2.13	1.96	1.96	2.28	2.74	2.43	1.82	1.98
Apatite	0.34	0.84	0.84	0.84	0.72	1.26	0.84	1.12	0.90	0.66	0.88	1.27	0.42	0.54	0.62
Water	0.67	0.71	0.70	0.64	0.72	1.26	0.84	1.12	0.90	0.66	0.88	1.27	0.42	0.54	0.62
Total	100.63	100.02	100.01	100.43	100.35	100.95	100.56	99.97	100.23	100.14	100.16	100.10	99.89	99.75	99.90

Classification:
Class, Order,
Range, Subrange

¹ Mean of 2 analyses. ² Corrected for sulfur (-0.02). ³ Received too late for inclusion in calculation in chap. 3. ⁴ Dried at 100° C. ⁵ Loss on ignition. ⁶ Spectrographic determination. ⁷ Corrected for sulfur (-0.01). ⁸ Also reported PbO, 0.002, and NiO, 0.001 (spectrographic determinations).

If the analysis was made in duplicate, the code number is marked with a footnote reference and the mean of the two analyses is given.

Tables 1 and 2 also give the petrographic "norm," computed from each analysis by the mineralogical staff of the Trace Elements Section of the Geochemistry and Petrology Branch, United States Geological Survey, under the direction of Theodore Botinelly. The CIPW norm is a conventional assignment of the elements in a rock to an arbitrarily designated set of "normative minerals," which may or may not actually be present in the rock. Rules for calculating the CIPW norm from the chemical analysis of a rock are given in textbooks of petrology and petrography (Johannsen, 1931, vol. 1, ch. 8). The norms are discussed in this report by Felix Chayes. (See pt. 5.)

The "consensus" of results is shown graphically in plate 1, where each analyst's result is shown by a point on the histograms for each constituent. Experience with collaborative analysis of other materials has shown that the correct values may be quite different from the most frequent ones. (Lundell, 1933.)

All collaborators did not report their analytical procedures. Examination of those results for which procedures were reported shows few regularities in relations between the methods and the results. At the present stage of the study it is not possible to estimate how much of the variation is caused by personal errors of the analyst, and how much by errors inherent in the procedures. It may be worth while, however, to describe briefly the course of a silicate rock analysis, pointing out tendencies to be high or low and their causes, and also to list the results by different methods of accomplishing the various steps of the analysis.

RESULTS OBTAINED BY DIFFERENT PROCEDURES

For many of the constituents one method was considerably more popular than others, and so the results of that method decide what is to be taken as a normal value. This is particularly shown in results for potassium, where weighing as K_2PtCl_6 is by far the most popular method. It is possible, of course, that a value far removed from the most popular range of values may be nearest the truth.

Silica (SiO_2).—Silica is determined by fusing the sample with sodium carbonate, dissolving the product in acid, usually HCl , and evaporating to dryness to dehydrate the silica and make it insoluble. After a single evaporation several milligrams of SiO_2 escape dehydration and remain in soluble form. A second dehydration recovers most of this, and the remainder can be recovered by dissolving the R_2O_3 group and dehydrating with H_2SO_4 . Perchloric and sulfuric acids are used by some analysts for second or third dehydrations.

Platinum or porcelain dishes are used for the evaporations; one analyst used pyrex beakers. With porcelain dishes results may be

low because of failure to remove all of the tightly adhering silica from the surface of the dish, or they may be high because of removal of the glaze. Two of the seven workers who used porcelain vessels for the dehydration took extraordinary precautions to remove all silica from the dish, and their results agree more closely than the rest with those obtained in platinum vessels. After the silica is collected, it must be ignited at sufficiently high temperature to assure complete dryness for weighing. The silica is then volatilized with HF, the crucible and residue weighed, and the weight of SiO_2 obtained by difference.

Results tend to be low, because negative errors due to failure to collect all SiO_2 generally are greater than positive errors from failure to drive off all water before weighing.

Processes used for determining SiO_2 on the two rocks are as follows (table 3):

1. Double dehydration with HCl only. This would tend to give low results because of failure to remove all silica.
2. Double dehydration with HCl, and recovery of SiO_2 in the R_2O_3 group. This should recover essentially all the SiO_2 .
3. Single dehydration with HCl, followed by a second dehydration with HClO_4 . This is generally considered a sound procedure although the results here reported are low.

Results of determinations of SiO_2 by these procedures are given in table 3.

TABLE 3.—Results with different methods of determining SiO_2 , in percent
[Numbers assigned to methods agree with numbers in text.]

Granite sample (G-1)			Diabase sample (W-1)		
Analyses by method indicated			Analyses by method indicated		
1. 2 HCl dehydrations only	2. 2 HCl dehydrations, recovery of SiO_2 in R_2O_3	3. 1 HCl dehydration; 1 HClO_4 dehydration	1. 2 HCl dehydrations only	2. 2 HCl dehydrations, recovery of SiO_2 in R_2O_3	3. 1 HCl dehydration, 1 HClO_4 dehydration
¹ 71.05	² 71.60	³ 71.68	¹ 51.28	² 52.09	³ 51.71
² 71.54	³ 71.88		² 51.38	³ 52.20	
³ 71.68	¹ 72.13		¹ 52.12	¹ 52.25	
³ 72.04	¹ 72.17		¹ 52.28	¹ 52.32	
¹ 72.19	¹ 72.23		¹ 52.31	² 52.38	
¹ 72.20	72.30		² 52.35	52.43	
¹ 72.34	¹ 72.34		² 52.42	52.45	
¹ 72.36	¹ 72.36		² 52.42	¹ 52.49	
² 72.46	¹ 72.40		¹ 52.45	¹ 52.51	
¹ 72.54	¹ 72.43		¹ 52.56	¹ 52.58	
² 72.54	72.45		² 52.66	¹ 52.59	
	72.46			¹ 52.59	
	72.46			52.61	
	¹ 72.48			53.01	
	¹ 72.52				
	¹ 72.55				
	¹ 72.68				
	¹ 72.74				

¹ Dehydration in platinum vessel.

² Dehydration in pyrex beaker.

³ Dehydration in porcelain vessel.

Alumina (Al_2O_3).—In most of the analyses alumina was calculated by subtracting from the R_2O_3 group—elements precipitated by neutralizing the acid solution with NH_4OH —the Fe_2O_3 , TiO_2 , and P_2O_5 . Unusual procedures and their results are as follows:

1. Separation of iron group from R_2O_3 by double precipitation with NaOH , reprecipitation with NH_4OH . Al_2O_3 was calculated by subtracting iron group from total R_2O_3 . TiO_2 and P_2O_5 were considered part of iron group. Percent alumina: granite sample (G-1), 14.13; diabase sample (W-1), 14.83.

2. Separation of iron group from R_2O_3 by double precipitation with KOH , reprecipitating with NH_4OH . Al_2O_3 was calculated by subtracting iron group and P_2O_5 from total R_2O_3 . P_2O_5 was considered not part of iron group. Percent alumina: granite sample (G-1), 13.18; diabase sample (W-1), 13.70.

3. Cupferron separation of Fe and Ti. Al_2O_3 and P_2O_5 were precipitated from filtrate and weighed. Percent alumina: granite sample (G-1), 14.49; diabase sample (W-1), 14.86.

Total iron (Fe).—Iron in solution, obtained either from the R_2O_3 or from a separate sample, is reduced to the ferrous state and titrated to the ferric state. An alternate to this process is to titrate from the ferric to the ferrous state with titanous ion. Essential variations in procedure have principally to do with the means of reduction. The different methods of reduction used are as follows:

1. Reduction of iron in HCl solution with stannous chloride (Zimmermann-Reinhardt method). Results are low if the titration is delayed owing to air-oxidation of ferrous ion, and they are high if titration is too rapid owing to oxidation of chloride ion to free chlorine if permanganate is used as oxidant.

2. Reduction with H_2S . Results are high if all H_2S is not removed.

3. Reduction with zinc amalgam. Sulfuric acid solution of iron is passed down a column of zinc amalgam (Jones' reductor) to reduce ferric ion to ferrous; this also reduces titanium ion. Titanium may be oxidized before the titration is made by aerating the solution, preferably in the presence of a trace of copper as catalyst. If this is not done, the results are high.

4. With silver reductor. Iron in HCl solution is reduced by passing the solution down a column of metallic silver. Titanium ion is not reduced and so does not interfere.

5. Reduction with SO_2 .

6. Titration of ferric ion with titanous ion.

Results by these methods of determining iron are given in table 4.

TABLE 4.—Results with different methods of determining total iron, in percent.

[Total Fe determined as Fe_2O_3 . Numbers of methods refer to text]

1. SnCl_2 reduction ¹	2. H_2S reduction ²	3. Zn amal- gam (Jones' reductor) ²	4. Silver reductor ¹	5. SO_2 reduction	6. Titration of ferric ion with titanous ion
Granite Sample (G-1)					
1.29	1.86	1.84	1.88	¹ 2.00	1.83
1.91	1.92	1.84	1.90		1.83
2.04	1.94	1.86	1.92		
2.34	1.99	1.91	1.84		
² 2.47	2.01	1.91	1.97		
	2.10	2.13			
	2.16	2.20			
	2.26	2.27			
	2.99				
Diabase Sample (W-1)					
11.03	10.97	10.70	10.95	¹ 11.33	11.21
11.10	11.08	10.96	10.97		
	11.10	11.11	11.13		
11.12	11.10	11.14	11.24		
² 11.18	11.17	11.21	11.66		
	11.56	11.23			
	11.82	11.36			
	11.93	12.19			

¹ Titration with $\text{K}_2\text{Cr}_2\text{O}_7$.² Titration with KMnO_4 .³ Titration method not stated.

Ferrous oxide (FeO).—The sample is dissolved in a mixture of sulfuric and hydrofluoric acids in a large crucible with tight-fitting lid; the crucible and its contents are placed in a large beaker containing dilute sulfuric acid, and usually boric acid, and the solution is titrated at once with standard oxidizing agent. Use of different oxidizing agents—for example, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ —for titrating the ferrous ion should not give differing results if they are properly standardized. Air oxidation during solution of the sample in HF is usually prevented by the steam generated (simple method) or by an atmosphere of CO_2 . Only three analysts definitely stated that they used a CO_2 atmosphere. Their results are: granite sample (G-1), 0.93, 1.04, and 1.05 percent; diabase sample (W-1), 6.80, 7.14, and 8.80 percent.

Calcium oxide (CaO).—Nearly all the reporting analysts precipitated calcium oxalate from the filtrate of the R_2O_3 separation and ignited it to the oxide. One analyst weighed calcium as CaSO_4 and reported: granite sample (G-1), 1.37 percent; diabase sample (W-1), 10.86 percent. Another laboratory determined calcium volumetrically by titrating the calcium oxalate, after solution in acid, with permanganate solution, reporting: granite sample (G-1), 1.57; diabase sample (W-1), 10.79 percent.

Magnesium oxide (MgO).—All reporting analysts precipitated magnesium as magnesium ammonium phosphate and weighed it as the pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

Sodium oxide (Na_2O).—A. Decomposition. No systematic differences are apparent in results from different methods of decomposition. Most reporting analysts decomposed the sample by sintering with a mixture of CaCO_3 and NH_4Cl —the J. Lawrence Smith procedure. Three analysts substituted BaCl_2 for NH_4Cl in the sinter mixture; this sinters more easily than the usual mixture, and automatically removes sulfate. Four analysts decomposed the samples with HF and H_2SO_4 . This should give a more complete recovery of alkalis, as it is a complete decomposition of the sample, while the J. Lawrence Smith procedure is an extraction. Of the four samples decomposed by the acid treatment, three were analyzed by the flame photometer.

B. Determination. Usually the mixed chlorides of potassium and

TABLE 5.—Results with different methods

GRANITE SAMPLE (G-1)

By difference from mixed chlorides			(4)	(5)	(6)	(7)
(1) K weighed as K_2PtCl_6	(2) K weighed as KClO_4	(3) K weighed as $\text{K}_2\text{NaCo}(\text{NO}_2)_6$	Weighed as Na_2SO_4	Weighed as sodium uranyl zinc acetate	By difference from mixed sulfates, K weighed as K_2PtCl_6	Flame photometer
Decomposed by J. Lawrence Smith method						
2.78	2.61	3.47		3.24	2.84	
3.13	3.04			3.30		
3.16				3.35		
¹ 3.18						
3.25						
3.26						
3.37						
3.41						
3.45						
3.48						
3.53						
3.54						
3.95						
Decomposed by J. Lawrence Smith method, using BaCl_2 instead of NH_4Cl						
3.59			3.26			3.27
Decomposed with HF and H_2SO_4						
3.29						3.35
						3.50
						3.78

¹ Weighed as platinum sponge.

sodium are weighed, the potassium is separated and weighed as (1) K_2PtCl_6 , (2) $KClO_4$, or (3) potassium cobaltinitrite, and the sodium obtained by difference. Sodium may also be weighed separately as (4) Na_2SO_4 , or (5) sodium uranyl zinc acetate. The determination may also be made (7) with a flame photometer. All these procedures may give good results when used by skilled analysts. One analyst reported (6) weighing the mixed sulfates and calculating the sodium by difference after weighing K_2PtCl_6 . The low solubility of Na_2SO_4 in alcohol may cause low results in this procedure owing to inclusion of Na_2SO_4 in the K_2PtCl_6 .

The three determinations made by method (2) and the one determination made by method (6) are low, but this is not evidence enough to establish any systematic error.

Results of determinations by the above seven procedures are given in table 5.

of determining Na_2O , in percent

DIABASE SAMPLE (W-1)

By difference from mixed chlorides			(4)	(5)	(6)	(7)
(1) K weighed as K_2PtCl_6	(2) K weighed as $KClO_4$	(3) K weighed as $K_2NaCo(NO_2)_6$	Weighed as Na_2SO_4	Weighed as sodium uranyl zinc acetate	By difference from mixed sulfates, K weighed as K_2PtCl_6	Flame photometer
Decomposed by J. Lawrence Smith method						
1.78 1.91 1.94 1.96 1.98 1.98 2.02 2.09 2.09 2.11 2.28 2.48 2.62	1.61	2.20		1.88 1.98 2.15	2.06	
Decomposed by J. Lawrence Smith method, using $BaCl_2$ instead of NH_4Cl						
			2.15			2.09
Decomposed with HF and H_2SO_4						
1.78						2.14 2.28 2.40

Potassium oxide, (K_2O).—A. Decomposition. Procedures were the same as for Na_2O , which is determined in the same portion of sample used for the K_2O determination. As with the determinations of Na_2O , there are no significant deviations associated with the modified decomposition procedures.

B. Determination. Potassium is weighed as (1) K_2PtCl_6 , (1a) platinum sponge separated from K_2PtCl_6 (Hicks' method), (2) $KClO_4$, or (3) potassium cobaltinitrite. One analyst reported (4) K_2PtCl_6 separated from solution of the mixed sulfates, a procedure that would give high results from inclusion of Na_2SO_4 in K_2PtCl_6 , due to low solubility of Na_2SO_4 in alcohol. The flame photometer (5) is an additional method.

One of the three determinations made by method (2) is low, and both of the determinations by method (4) are high, but this is not enough evidence to establish systematic error.

TABLE 6.—Results with different

GRANITE SAMPLE (G-1)

(1) As K_2PtCl_6 from mixed chlorides	(2) As $KClO_4$	(3) As $K_2NaCo(NO_2)_6$	(4) As K_2PtCl_6	(5) Flame photometer
Decomposed by J. Lawrence Smith method				
4.48	3.85	5.54	6.88	
5.30	5.86			
5.34				
5.42				
5.46				
5.46				
5.47				
5.49				
5.50				
5.52				
¹ 5.52				
5.56				
5.62				
5.74				
5.74				
5.84				
6.23				
Decomposed by J. Lawrence Smith method, using $BaCl_2$ instead of NH_4Cl				
4.99				5.30
5.55				
Decomposed with HF and H_2SO_4				
5.37				5.44
				5.51
				5.64

¹ Weighed as platinum sponge.

Results of determinations of K_2O by different procedures are given in table 6.

Determination of alkalis by flame photometer.—Additional work on alkali determinations with the flame photometer is reported in part 3, table 16.

Phosphorus pentoxide (P_2O_5).—Phosphate is separated from nitric acid solution by precipitation as ammonium phospho-molybdate. The precipitate can be (1) weighed directly, (2) converted to $Mg_3P_2O_7$ and weighed, (3) converted to $PbMoO_4$ and weighed, or (4) determined volumetrically by alkalimetric titration. All four methods give good results. One analyst (5) converted to $P_2O_5.24MoO_3$ by heating at 500 C before weighing (method of Woy; Dittler, *Gesteinsanalytisches Praktikum*, Berlin & Leipzig, Walter de Gruyter & Co., 1933, pp. 54–56).

methods of determining K_2O , in percent

DIABASE SAMPLE (W-1)				
(1) As K_2PtCl_6 from mixed chlorides	(2) As $KClO_4$	(3) As $K_2NaCo(NO_2)_6$	(4) As K_2PtCl_6	(5) Flame photometer
Decomposed by J. Lawrence Smith method				
0.41 .54 .57 .58 .60 .60 .62 .64 .65 .66 .67 1.74 .75 .82 .82 .84 1.17	0.66	0.60	1.30	
Decomposed by J. Lawrence Smith method, using $BaCl_2$ instead of NH_4Cl				
0.71				0.60
Decomposed with HF and H_2SO_4				
0.64				0.66 .68 .69

Results of determinations of P_2O_5 are given in table 7.

TABLE 7.—Results with different methods of determining P_2O_5 , in percent

(1) Weighed as (NH_4) ₃ PO ₄ , 12MoO ₃	(2) Weighed as Mg ₂ P ₂ O ₇	(3) Converted to PbMoO ₄ and weighed	(4) Volumetric	(5) Weighed as P ₂ O ₅ .24MoO ₃
Granite sample (G-1)				
0.03 .04 .08 .08 .08 .08 .09 .10 .14	0.08 .08 .08 .08 .09 .09 .10 .10 .11 .12 .12 .16 .27 .41	0.10	"Traces" 0.06 .09 .12 .20	0.10
Diabase sample (W-1)				
0.06 .11 .13 .13 .14 .16 .18 .18	0.08 .11 .12 .13 .13 .13 .14 .15 .16 .17 .22	0.10	0.08 .13 .15 .17 .18	0.10

Manganese oxide (MnO).—The small percentages of manganese in the granite and diabase were determined colorimetrically after oxidizing the manganese to permanganate using (1) periodate, (2) bismuthate, or (3) persulfate in the presence of silver ion as catalyst. Four reporting analysts determined manganese volumetrically, after oxidizing to permanganate with persulfate and silver ion, by adding an excess of ferrous sulfate and titrating the excess with standard solution of oxidizing agent. It is possible to get good results by all four methods.

Results of determinations of MnO by the different methods are assembled in table 8. Some of the results are so aberrant as to suggest the possibility of arithmetical errors in the dilution factors used.

TABLE 8.—Results with different methods of determining MnO

Colorimetric method			(4) Persulfate (volumetric method)
(1) Periodate	(2) Bismuthate	(3) Persulfate	
Granite sample (G-1)			
0.01	0.02	0.02	0.02
.02	.02	.02	.03
.02	.03	.03	.03
.02	.04	.05	.04
.02			
.03			
.03			
.03			
.03			
.03			
.03			
.03			
.03			
.03			
.04			
Diabase sample (W-1)			
0.13	0.11	0.12	0.13
.16	.17	.12	.16
.16	.20	.18	.18
.16		.23	.26
.16			
.17			
.17			
.17			
.17			
.18			
.18			
.21			
.21			
.22			
.53			

Titania (TiO_2).—Titania was invariably determined colorimetrically after oxidation to the amber color by peroxide in sulfuric acid solution containing phosphoric acid to reduce color due to ferric ion. The results reflect the care and skill of the analyst rather than differences of method. As with manganese, blunders in dilution factors are suspected in some of the results.

Total water.—Uncombined water (H_2O —) was invariably taken as the percentage loss in weight at 105 to 110° C. For total water, from which combined water (H_2O +) is calculated by subtracting

H₂O—, a number of methods were used: (1) Loss on ignition, corrected for oxidation of ferrous oxide. If FeO is not completely oxidized to Fe₂O₃, the results obtained are high; (2) volatilization and isolation in a Penfield tube without a flux; (3) the Penfield tube method using anhydrous sodium tungstate, Na₂WO₄, as a flux to decompose the sample; (4) the Penfield tube with basic lead chromate as a flux; (5) the Penfield tube with lead oxide as a flux; and (6) volatilization and the absorption of water in a desiccant.

Results of determinations of total water using these methods are given in table 9.

TABLE 9.—Results with different methods of determining total water (total H₂O), in percent

[Numbers in box heads refer to text]

(1) Ignition loss (corrected for FeO oxidation)	(2) Penfield (no flux)	(3) Penfield (basic lead chromate flux)	(4) Penfield (PbO flux)	(5) Penfield (Na ₂ WO ₄ flux)	(6) Volatiliza- tion and absorption
Granite sample (G 1)					
0.52	0.20	0.35	0.36	0.27	0.36
.53	.23		.37	.34	.43
.63	.27		.38	.36	.49
.78	.32		.40	.42	.52
	.34			.42	
	.36				
	.36				
	.40				
	.43				
	.47				
	.52				
	1.44				
Diabase sample (W-1)					
0.88	0.38	0.72	0.64	0.59	0.69
1.12	.42		.64	.59	.80
1.26	.44		.66	.62	.90
	.56		.66	.64	
	.57				
	.62				
	.64				
	.66				
	.66				
	.71				
	.84				
	.89				
	1.26				

Summation.—The traditional practice of inspecting the summation of a rock analysis is a necessary test of its correctness, but a summation near to 100.0 percent is no assurance of its correctness. For example, several analyses may be seen to have very low results for silica, although their summations are satisfactory.

TABLE 10.—“Good” summations with low-silica results

Sample material	Analyst No.	SiO ₂ (percent)	Summation (percent)
Granite (G-1)-----	{ 15	71.68	100.01
	{ 16	71.05	100.00
Diabase (W-1)-----	{ 11	51.71	100.06
	{ 15	51.38	100.04

Elements seldom determined.—Some analysts reported in one or both rocks determinations of elements commonly ignored. By chemical methods barium was determined by five analysts, sulfur was determined by seven, strontium, lithium, and chromium by two, and zirconium by one of the analysts. One analyst determined all these elements except sulfur, and in addition lead and nickel, spectrographically. The foregoing includes those who reported “none” or 0.00 percent. A special comparative study of the rarer elements in the granite and diabase samples is reported in Part 4 of this report.

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A COOPERATIVE INVESTIGATION OF
PRECISION AND ACCURACY IN
CHEMICAL, SPECTROCHEMICAL, AND MODAL ANALYSIS OF
SILICATE ROCKS

**PART 3. SPECTROCHEMICAL ANALYSIS OF MAJOR
CONSTITUENT ELEMENTS IN ROCKS
AND MINERALS**

BY W. H. DENNEN, L. H. AHRENS, AND H. W. FAIRBAIRN ⁴

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• INTRODUCTION

Spectrochemical analysis has long been recognized as a sensitive and rapid method of qualitative analysis for some 70 elements, and as an invaluable quantitative method for these elements at low concentrations. Its application in this respect has been particularly valuable in geology. With the marked improvement in the precision and accuracy of spectrochemical methods during the past 2 decades attention has been drawn to its possible use for the quantitative analysis of the major constituent elements. The question of course arises as to whether any useful purpose would be served by using spectrochemical procedures. For minor constituent analyses the reason is obvious, but for the major constituents chemical analysis has served us well. In attempting to answer the question a few points should be borne in mind.

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1. Spectrochemical analysis is much more rapid than chemical analysis, and because of this it becomes possible to investigate many geological problems which one would hesitate to attempt were only the relatively slow chemical procedures available—see for example discussion of various geological applications by Ahrens (1950, ch. 23).

2. The precision and accuracy of spectrochemical analysis is reasonably high, comparing favorably with chemical methods.

3. The cost of a quantitative spectrochemical analysis is small compared with that of a chemical analysis.

4. The spectrum of a specimen provides a permanent record of the presence of several other elements that may be of interest. Thus it is possible to determine several major constituent elements and also a number of minor ones from a single spectrogram.

5. Where material for analysis is difficult to prepare, as in many mineralogical investigations, the small sample required for spectrochemical analysis—as little as 3 mg is sufficient—is a considerable advantage over chemical analysis.

Bearing in mind these points, it is clearly evident that quantitative spectrochemical analysis offers some definite advantages, provided that both precision (reproducibility) and accuracy (degree of approach to the absolute value) are adequate. First we will discuss the precision and accuracy of spectrochemical methods in general; secondly, we will record some observations and provide statistical data on some major constituent analyses, mainly on the diabase and granite provisional standards, as a basis of comparison with chemical methods.

PRECISION (REPRODUCIBILITY) IN SPECTROCHEMICAL ANALYSIS

Many sources of excitation are used in spectrochemical analysis. For the analysis of minerals, rocks and related materials the direct-current arc is most commonly employed and the discussion here applies to this source in particular. Many reports in the literature describe the arc method as “semi-quantitative.” These reports, which are unfortunately misleading, at one time caused the direct-current arc method to lapse into disrepute, from which, however, it has strongly recovered. Unlike many other sources, however, the choice of an internal standard is usually very critical and much depends, therefore, upon the internal standard used and on the smoothness of the arc burn. (For discussion on internal standardization in the direct-current arc, see Ahrens (1950), ch. 7.) Provided an ideal internal standard has been used, meticulous care has been given the various operational details, and conditions in general are ideal, a reproduc-

bility of 2 percent, expressed as relative deviation, may be attained. In practice, this value is frequently approached and relative deviations of 3 to 5 percent are quite commonly obtained (tables 11, 12, 13); occasionally relative deviations of 2 to 3 percent are reported.

The following summarizes the statistical terminology used in this chapter.

n , number of observations, analyses, etc.

\bar{x} , arithmetic mean.

d , deviation of an observation from the mean.

s , standard deviation = $\sqrt{\frac{\sum d^2}{n-1}}$, the uncertainty of a single observation.

$s_{\bar{x}}$, standard error = $\frac{s}{\sqrt{n}}$, the error of the arithmetic mean.

C , relative deviation = $\frac{s}{\bar{x}} \times 100$, also known as the coefficient of variation.

E , relative error = $\frac{C}{\sqrt{n}}$.

The quantities C and E permit comparison of data on a percentage basis, which is not possible if s and $s_{\bar{x}}$ only are used.

Accuracy in spectrochemical analysis

Spectrochemical methods of powder analysis are particularly liable to systematic error (bias). Such an error has several causes (see Ahrens, 1950, ch. 8) and is associated with the fact that the general physical and chemical composition of a specimen influences the intensity of line emission. Error due to compositional variation may be introduced where synthetic standards have to be used—usually causing a systematically high result in the naturally occurring unknowns—and when the mineralogical and chemical composition of the unknowns varies greatly. If systematic error is absent in a precise method, the method will then be accurate.

Error due to the use of synthetic standards may be overcome by using naturally occurring standards that have been carefully analyzed chemically. For the major constituents this procedure may invariably be employed, but for relatively rare elements it is usually impossible. This is one use of the diabase and granite standards described in part 1. The second source of error—wide variation in the general composition of the unknown—would appear if the standard diabase and granite were used as standards for the analysis of markedly different rock types. To overcome errors of this type it is probably safest to use a separate batch of standards for each composition type;

TABLE 11.—Relative deviation (C) and relative error (E) for Al_2O_3 , Fe^o , MnO , and CaO

[All measurements by W. H. Dement. Lines used in observations: Sr, 2931 (internal standards); Mg, 2778; Fe, 2929; Al, 2652; Mn, 2801; Ca, 3006 and 3158. Italicized figures indicate poor results attributable to very low or very high line intensities. Figures in parentheses indicate values determined spectrographically.]

Sample material	Reference No.	Num-ber of obser-vations	Constituents											
			Al_2O_3			Fe^o			MnO			MgO		
			Concen-tration (percent)	C	E	Concen-tration (percent)	C	E	Concen-tration (percent)	C	E	Concen-tration (percent)	C	E
Granite	Q-1	9	14.44	4.7	1.6	1.44	4.7	1.6	0.03	12.4	4.1	0.30	1.42	1.5
Dabase	W-1	12	15.53	5.3	1.7	7.88	6.2	1.8	0.19	9.0	2.6	6.32	10.95	1.7
Granite	R-22	12	17.51	5.3	1.7	4.20	3.9	1.8	(.34)	4.1	2.2	(.42)	(1.7)	1.7
Obsidian	R-280	27	12.64	5.5	2.5	1.88	5.4	2.4	.03	4.9	4.1	.04	.59	2.8
Limestone	BS 18	4	4.16	5.0	2.5	1.14	5.0	2.5	.038	3.6	1.8	2.19	41.32	4.0
Clay	BS 98	5	25.54	7.9	3.5	1.43	3.4	1.5	.005	10.6	4.7	.72	.21	3.2
Bauxite	BS 76	5	37.7	6.8	3.0	1.67	7.4	3.3	(.001)	7.6	3.4	(.5)	(.5)	2.8
Glass	BS 93	5	1.94	5.4	2.4	.063	14.0	6.3	.16	8.4	3.7	.026	(.16)	3.7
Olivine	R-1579	5	1.07	22.3	10.0	8.72	3.9	1.8	.10	1.3	1.6	46.27	36	1.7
Pyroxene	R-1096	5	3.67	4.0	1.8	3.25	2.6	1.2	.14	2.5	1.1	18.28	20.33	3.3
Amphibole	R-1110	5	11.33	3.5	1.6	10.45	4.0	1.8	.19	5.4	2.4	12.41	12.03	1.5
Biotite	R-1578	5	14.58	4.3	1.9	8.17	5.3	2.4	(.01)	12.5	6.3	11.84	(.07)	2.6
Microcline	BS 70	4	18.03	3.6	1.8	.21	37.2	16.6	.0003	11.5	5.8	.013	13.5	6.8
Albite	BS 99	4	19.06	6.5	3.1	.47			.0003	11.5	5.8	.33	5.6	2.8

Fe^o indicates total Fe as metallic iron.

for example, one for granitelike rocks, one for gabbroic types, one for ultramafics, and one each for feldspar, mica, pyroxene, and so on. This will of course necessitate building up a large collection of accurately analyzed rock and mineral types. The same procedure may be applied to soil types.

TABLE 12.—*Reproducibility data for SiO₂ in diorite*

[All measurements by Lorraine G. Gorfinkle. Lines used in observations: Be, 2494 (internal standard); Si, 2528. Computations: \bar{x} , 62.5; s , 2.19; C , 3.5; $S\bar{x}$, 0.50; E , 0.80]

Analysis No.	Concentration (percent)	Analysis No.	Concentration (percent)	Analysis No.	Concentration (percent)
1.....	61.5	7.....	61.0	13.....	63.8
2.....	63.0	8.....	62.0	14.....	63.4
3.....	59.7	9.....	63.8	15.....	60.2
4.....	66.5	10.....	62.5	16.....	58.7
5.....	63.8	11.....	64.7	17.....	63.0
6.....	61.0	12.....	66.9	18.....	62.5

TABLE 13.—*Spectrochemical precision data for Na₂O and K₂O (five analyses each) in granite sample (G-1)*

Na ₂ O	K ₂ O ¹	Na ₂ O	K ₂ O ¹
3.30.....	5.57	3.39.....	5.28
3.32.....	5.50	3.45.....	5.64
3.24.....	5.30		

¹ One extremely low analysis of 4.25 percent was discarded from this group.

NOTE.—All measurements by Margaret Kearns, Department of Geology, Massachusetts Institute of Technology. Lines used in observations: Li, 4973 (internal standard); Na, 5882; K, 6939. Computations: Na₂O: \bar{x} , 3.34; C , 2.55; E , 1.14; K₂O: \bar{x} , 5.46; C , 2.95; E , 1.32.

Another approach to the elimination of error due to compositional variation is the use of a compound which acts as a flux and buffer. The fluxing action breaks down mineral structure and quickly converts all the powder to a melt, while buffer action aids in keeping arc temperature constant. To buffer successfully, the metal in the buffer compound should have a relatively low ionization potential. Li₂CO₃ has been used for this purpose, and germanium metal may also be employed (Strock, 1948).

Apart from the use of chemically analyzed, naturally occurring standards, there are other factors which tend to improve over-all accuracy of a major-constituent analysis when compared with a minor-element analysis. Fundamentally, of course, there is no difference and no sharp dividing line. All spectrochemical methods are based on the same principle, namely, the variation of line intensity with the concentration of emitting atoms in the source. In minor-element techniques, however, much emphasis has to be placed on developing a method that will provide the utmost sensitivity so as not to overlook a trace of elements, and in so doing quantitative

reproducibility may be impaired. This does not hold for major-constituent analyses. There is usually much sensitivity to spare and nearly all attention can be focused on developing a very smooth-burning and reproducible arc. A high dilution in an appropriate matrix—powdered graphite or carbon, CuO, or NiO, for example— aids in this respect and also tends to improve accuracy by buffering—this would not apply to carbon because of its high ionization potential—and by reducing selective volatilization (fractional distillation) differences. Furthermore, relatively small anodes may be used for holding the specimen and through their use the reproducibility of the arc method can sometimes be improved. This does not apply to cathode-layer excitation where small cathodes must in any case be used for holding the specimen in order to obtain proper cathode-layer enrichment.

Several methods have been described for the spectro-chemical analysis of major constituents in minerals, rocks and allied materials, using the direct-current arc. In the sections which follow we will present data on reproducibility and discuss the accuracy of working curves for certain elements, using (a) a method described by Kvalheim (1947) which has been modified in a few minor respects for the analysis of Ca, Mg, Fe, Mn, Al, and Mg; (b) a method modified after Kvalheim (1947) for silicon; and (c) a method developed in the Cabot Spectrographic Laboratory, Massachusetts Institute of Technology, for the analysis of Na and K.

The reader may obtain further information on the reproducibility of these and other spectrochemical methods of major-element analysis by referring to the bibliography given by Ahrens and others (1952?).

PROCEDURE AND PRECISION IN DETERMINATION OF Ca, Al, Mg, Mn, AND Fe

Only a brief outline of the above method for determination is given here. Details may be obtained by reference to Ahrens and others (1950).

In a procedure slightly modified after Kvalheim (1947) strontium is used as the internal standard for the determination of the above elements. This internal standard appears generally suited to the analysis of the above group of elements. Kvalheim also employed it for Na and K, but because of the much greater volatility of the alkali metals, strontium is usually not an ideal internal standard for them. Using Kvalheim's procedure we found a poorer precision for the alkali metals than for the above elements. Consequently, a separate procedure was developed for the alkali metals. (See p. 31.)

Reproducibility data giving relative deviation and relative error in analyses are shown in table 11. In general, the relative deviations are

reasonably satisfactory. Relatively poor reproducibility in determination of Al in olivine and Fe and Ca in plagioclase is attributed to the low concentration of these elements. This has caused a marked weakening of the analysis lines and makes microphotometry less accurate. This error could undoubtedly be reduced by using some other more intense lines at the low concentrations.

The materials listed in table 11 were chosen in order that the effect of different matrices might be observed. The results show that a change of matrix composition has no apparent effect on the precision. Matrix composition might, however, introduce a systematic error, but the plotted points in figures 4 to 7 do not appear to show any effect of composition for the specimen types investigated. The point should be explored further, however, and if one were in doubt the safest procedure would be to employ separate standards for each unknown type.

PROCEDURE AND PRECISION IN DETERMINATION OF SILICON

The method described by Kvalheim (1947) using beryllium as the internal standard gives a relatively high precision provided, as described by Ahrens and others (1950), the sample is greatly diluted with carbon. Much dilution with carbon serves to make the volatilization rates of beryllium and silicon almost identical; otherwise beryllium is much less volatile.

The reproducibility data given in table 12 refer to a specimen of diorite. They apply generally to all rocks in the range of 5 to 100 percent SiO_2 . This wide range in silicon concentration can be handled with equal precision because there are several closely-spaced silicon lines of varying intensity at the analyst's disposal. These measurements were made before diabase (W-1) and granite (G-1) were available for comparison.

PROCEDURE AND PRECISION IN DETERMINATION OF Na AND K

A satisfactory spectrochemical method for the analysis of Na and K in rocks is of considerable value, first because an analysis for alkali metals necessitates a separate operation—usually a J. Lawrence Smith fusion—and secondly, because chemical reproducibility may be poor, particularly at relatively low concentrations—potassium in diabase, for example (fig. 2A). A method has been developed at the Cabot Spectrographic Laboratory, Massachusetts Institute of Technology (see Ahrens and others, 1952?), which provides a satisfactory precision and accuracy for Na and K in most silicate rocks; with little extra

effort the other alkali metals, Li, Rb, and Cs may be determined with about equal precision. All alkali metals behave much in the same way in the arc, and highest accuracy is usually attainable when one alkali metal is used as an internal standard for another; this forms the basis of the spectrochemical procedure which has been developed.

Spodumene is added to each specimen as a source for lithium, which is the internal standard. Sodium may be determined over a concentration range of about 0.5 to 15 percent. For potassium, lithium is used as the internal standard for relatively high concentrations (more than 3 percent). Below this concentration use is made of a double procedure. Sodium is first determined in the usual way, using lithium as the internal standard. The specimen—the same portion—is then arced using a different procedure, in which sodium is used as a variable internal standard. In this second procedure potassium may be determined down to 0.5 percent and Li, Rb, and sometimes Cs may be determined accurately at the same time.

Table 13 shows some typical reproducibility data for sodium and potassium in the granite specimen. The relative error for sodium is about 2.5 percent, which is highly satisfactory; the relative error for potassium, is about 3.5 percent. At lower concentrations of potash, for which the double procedure is used, the relative error is about 6 percent.

STATISTICAL ANALYSIS OF THE CHEMICAL DATA

In the preceding chapter the chemical data for the two provisional standards are given and the procedures used by the analysts are tabulated and discussed in some detail. The data are there presented as histograms. It was concluded that differences in methods of analysis could not explain the dispersion of values obtained. Additional discussion of these analyses is now desirable in order to test their usefulness for calibration of the spectrochemical investigation.

EXPLANATION OF FIGURES 1 AND 2

Histograms based on chemical data of tables 1 and 2 and table 14. Vertical scale showing frequency is similar throughout—one block equals one analysis. The class interval shown by the horizontal scale is an arbitrary fraction of the mean and is given for each figure. The numbers at the ends of each histogram are the lowest and highest values reported for each constituent. The intermediate number is the arithmetic mean, placed approximately at its correct position in the histogram. The cross-lined blocks at the ends of some of the histograms represent those analyses which on statistical grounds alone could reasonably be rejected (see p. 43).

FIGURE 1.—A, Class interval for SiO_2 is 0.5 percent of the arithmetic mean; that for Al_2O_3 is 1 percent. B, Class interval for Fe° , FeO , and Fe_2O_3 is 5 percent of the respective arithmetic means. C, Class interval for CaO and MgO is 5 percent of each arithmetic mean.

FIGURE 2.—A, Class interval for Na_2O and K_2O is 5 percent of each arithmetic mean. B, Class interval for MnO and P_2O_5 is 33.3 percent of each arithmetic mean. C, Class interval for TiO_2 and H_2O is 10 percent of each arithmetic mean.

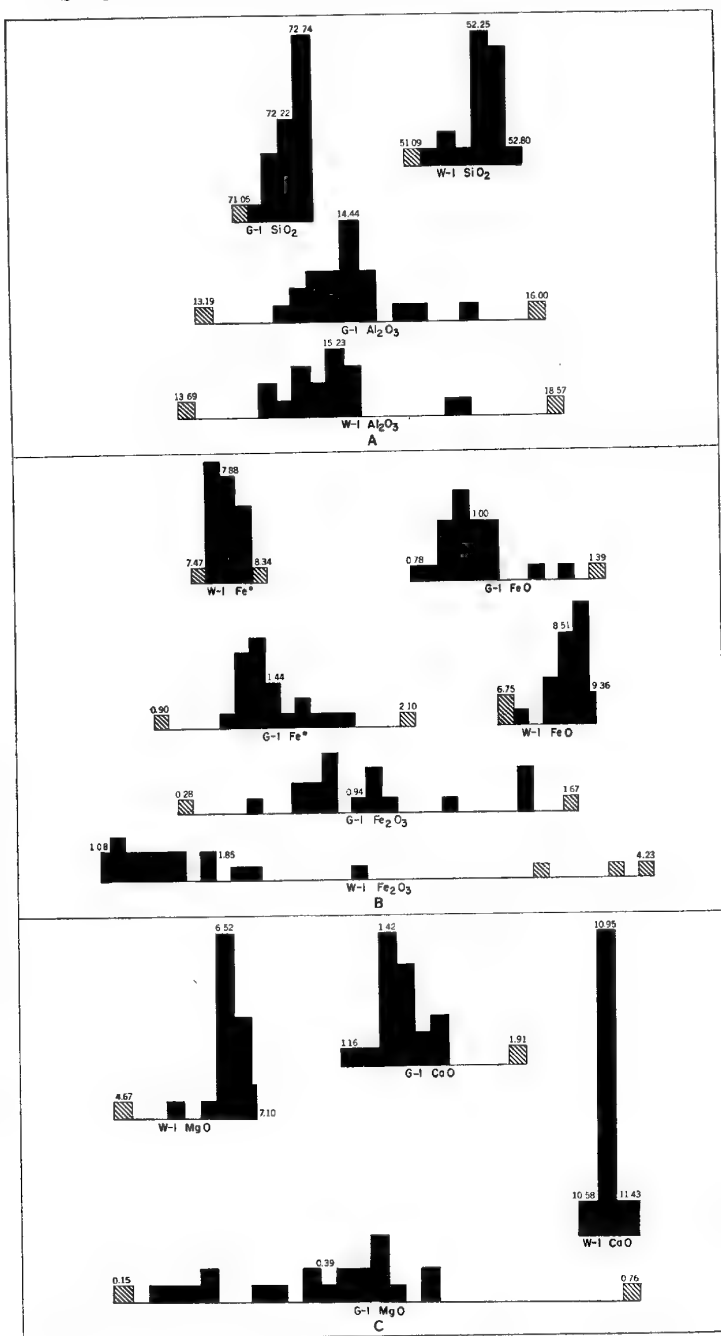


Figure 1.

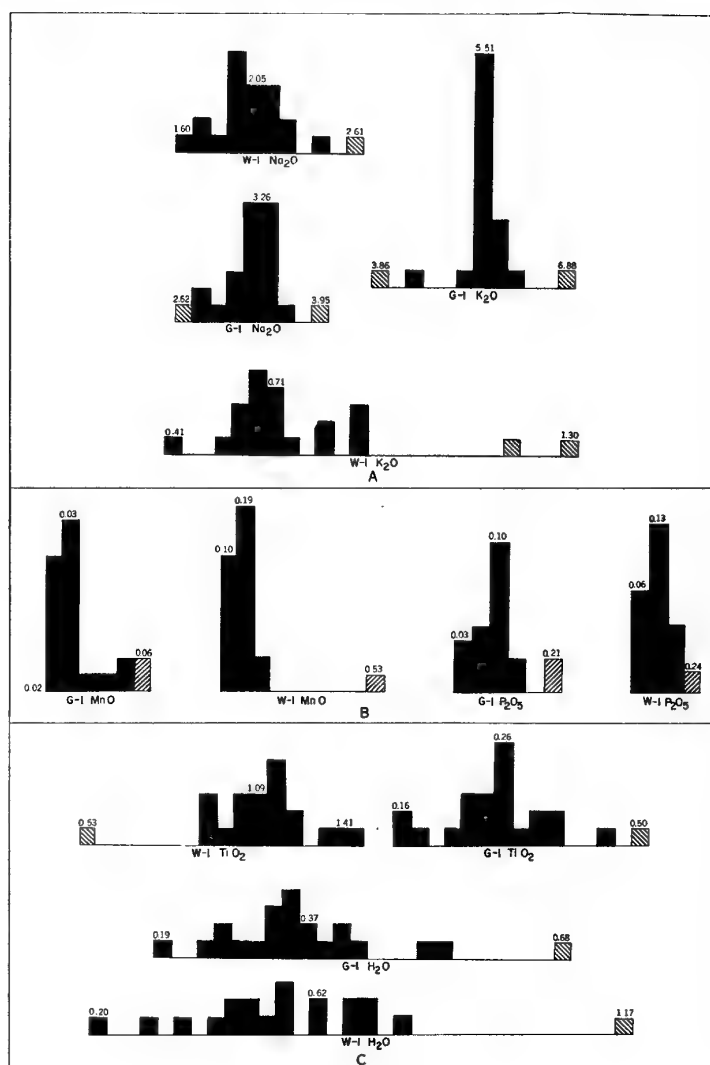


Figure 2.

In the histograms of part 2 (pl. 1) the class interval is 0.1 percent regardless of the concentration of the constituent—MnO in granite excepted. All analyses are included in this compilation, irrespective of the number from any given laboratory. Another method of presenting the chemical data is shown in figures 1 and 2 (pt. 3). The class interval in each histogram is fixed at some convenient percentage of the mean—5 percent for most—and only one value from each laboratory is included—the mean, where more than one analyst per laboratory made an analysis. Analyst 34 reported too late to be included in these calculations. This method of determining class interval allows direct visual comparison of the granite and diabase for any one constituent and, for constituents plotted with the same class interval, direct comparison of the dispersion of different constituents. The “laboratory mean” method prevents undue weighting of the histograms in favor of laboratories which furnished a number of analyses. This may be an important factor where, as in this investigation, the chemical results were intended as calibration for the spectrochemical data.

The high degree of dispersion shown in the histograms for some constituents casts immediate doubt on their usefulness for calibration purposes. The means commonly do not coincide with the highest-frequency columns and only one histogram (CaO in diabase standard, W-1) shows a symmetrical distribution of values on either side of the mean. The problem is similar to that encountered by Larsen (1938) in his smaller-scale study of replicate amphibole analyses.

Statistical data are assembled in table 14 and include the standard deviation, standard error, and relative error for each constituent. For most of the constituents the relative error of the mean varies inversely with the magnitude of the mean. That is, the relative error (E) for CaO in the diabase (10.95 percent CaO) is lower than in the granite (1.42 percent CaO). These relations are shown in figure 3. The exceptions, shown by Al_2O_3 , Fe_2O_3 , MnO and H_2O , are of less significance than the trend followed by the majority. Petrologists who make use of chemical data may study this figure with much profit to themselves. Low error with high concentration, and high error with low concentration are taken for granted by chemists, but are little appreciated by petrologists.

In fairness to analytical chemists, it should be said that much greater precision can be obtained than that shown in table 14 if a

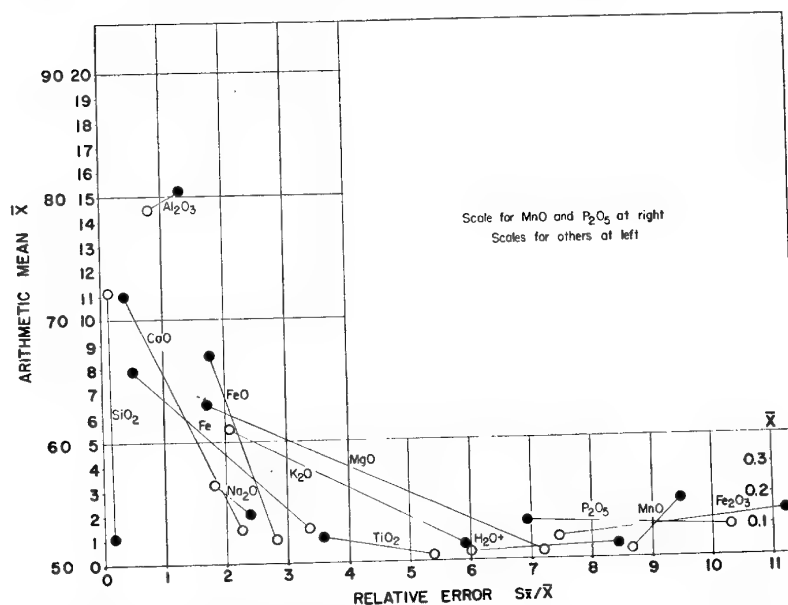


FIGURE 3. Diagram showing mutual relations of the arithmetic mean and relative error for each constituent in the two standard rocks—filled circles, W-1; open circles, G-1. The lines connecting W-1 and G-1 for each constituent draw attention to the inverse relation of the mean and the relative error—high concentration and low error; low concentration and high error—which holds for most of the constituents.

careful selection of analysts is made and special precautions are taken. For example, the accompanying table 15 shows admirable precision for certain constituents in a soda feldspar analyzed by the Bureau of Standards and their collaborators. For every constituent E is superior to its counterpart in table 14, after making due allowance for the relative concentration levels. This restricted type of test was not desired for the granite and diabase analyses and is quoted here as a reminder that the procedures used by analytical chemists are capable of high precision and accuracy.

STATISTICAL ANALYSIS OF FLAME PHOTOMETER DATA FOR ALKALI METALS

The increasing use of the flame photometer for routine determination of Na and K makes it advisable to include some results on the two standard rocks. In addition, determinations have been made on two standard samples of feldspars from Bureau of Standards. The data at hand are listed in table 16. For the two standard rocks the E values for the alkali metals (table 14) obtained from 24 laboratories

are much inferior to the flame-photometer values; for the soda feldspar (albite sample, BS 99) the precision of the Bureau of Standards chemists (table 15) is somewhat better than the flame photometer for Na_2O , but the reverse is true for K_2O .

RELATIVE PRECISION OF CHEMICAL AND SPECTRO-CHEMICAL ANALYSIS

A thorough comparative test of reproducibility in chemical and spectrochemical analysis has not yet been made. The comparison presented in table 18 is based on chemical determinations, shown in table 17, by seven analysts from a single laboratory and on spectrochemical determinations by two analysts, also from a single laboratory. The chemical determinations are included in the histograms of part 2 and were made by analysts of the United States Geological Survey. Table 17 gives the mean, the standard deviation, and the relative deviation for each constituent in the two standard rocks. The relative deviation is large where the concentration of the constituent is low, as in MnO and P_2O_5 , and small where the concentration is high, as in SiO_2 . Table 18 compares those constituents which have been investigated by spectrochemical means. It is to be particularly noted that the chemical rule relating to concentration and precision (fig. 3 and table 17) does not hold for spectrochemical analysis, in which reproducibility is essentially independent of concentration. Spectrochemical precision is therefore usually superior to chemical where concentration is low but is inferior where concentration is high. (See "remarks" column in table 18.)

TABLE 14.—*Precision of determinations in rock analyses by 24 laboratories*¹

[Computations: \bar{x} , arithmetic mean; s , standard deviation; $s_{\bar{x}}$, standard error; E , relative error]

	Granite (G-1)				Diabase (W-1)			
	\bar{x}	s	$s_{\bar{x}}$	E	\bar{x}	s	$s_{\bar{x}}$	E
SiO_2	72.22	0.43	0.09	0.125	52.25	0.41	0.09	0.167
TiO_226	.067	.01	5.38	1.09	.179	.04	3.59
Al_2O_3	14.44	.541	.11	.79	15.23	.938	.20	1.31
Fe_2O_394	.34	.07	7.45	1.85	.953	.21	11.24
FeO	1.00	.135	.03	2.81	8.51	.707	.15	1.77
Fe° ²	1.44	.231	.05	3.35	7.88	.180	.04	.50
MnO03	.0122	.003	8.66	.19	.086	.02	9.47
MgO39	.135	.03	7.20	6.52	.520	.11	1.70
CaO	1.42	.152	.03	2.25	10.95	.197	.04	.38
Na_2O	3.26	.284	.06	1.81	2.05	.230	.05	2.39
K_2O	5.51	.549	.11	2.07	.71	.196	.04	5.89
H_2O^+37	.104	.02	6.00	.62	.245	.05	8.42
P_2O_510	.045	.01	10.3	.13	.0414	.01	6.93

¹ Analyses recalculated to 100 percent, omitting H_2O —.

² Fe° indicates total Fe as metallic iron. Percent not included in summation.

TABLE 15.—*Precision of determinations in six partial chemical analyses of soda feldspar (BS99) from six laboratories*¹[Computations: \bar{x} , arithmetic mean; s , standard deviation; s_x , standard error; E , relative error]

	\bar{x}	s	C	E		\bar{x}	s	C	E
SiO ₂	68.66	0.047	0.07	0.03	Na ₂ O	10.73	0.059	0.55	0.24
Fe ₂ O ₃67	.004	6.5	2.9	K ₂ O41	.025	6.2	2.8
CaO36	.002	6.1	2.7					

¹ U. S. Bureau of Standards analyses, issued 1931.TABLE 16.—*Precision of determinations in four analyses of alkali metals by flame photometer*All measurements by Geraldine Sullivan, Department of Geology, Massachusetts Institute of Technology.
Computations: \bar{x} , arithmetic mean; C , relative deviation; E , relative error]

Material	Reference No.	Number of observations	Na ₂ O			K ₂ O		
			\bar{x}	C	E	\bar{x}	C	E
Granite	G-1	8	3.58	1.40	0.50	5.42	0.83	0.29
Diabase	W-1	8	2.29	2.85	1.01	.693	2.28	.81
Microcline	BS70	5 and 8	2.33	1.73	.71	12.42	1.38	.49
Albite	BS99	5 and 7	10.75	1.39	.62	.504	5.57	2.10

TABLE 17.—*Precision of determinations in replicate rock analyses by one laboratory (U. S. Geological Survey)*[Analyses recalculated to 100 percent, omitting H₂O—. Computations: \bar{x} , arithmetic mean; s , standard deviation; C , relative deviation]

	Granite, G-1 (7 analysts)			Diabase, W-1 (6 analysts)		
	\bar{x}	s	C	\bar{x}	s	C
SiO ₂	72.64	0.23	0.31	52.66	0.34	0.64
TiO ₂25	.03	11.2	1.03	.04	4.15
Al ₂ O ₃	14.13	.17	1.22	14.87	.48	3.23
Fe ₂ O ₃86	.17	19.3	1.41	.47	33.4
FeO	1.06	.06	5.72	8.91	.16	1.82
Fe ^o	1.43	.13	9.30	7.91	.31	3.92
MnO03	.01	30.5	.17	.03	15.6
MgO44	.04	9.90	6.51	.40	6.00
CaO	1.34	.09	6.53	10.95	.09	.83
Na ₂ O	3.43	.21	6.23	2.20	.13	5.72
K ₂ O	5.43	.21	3.83	.68	.05	7.06
H ₂ O+31	.08	26.7	.45	.05	10.5
P ₂ O ₅10	.02	23.4	.15	.03	18.7

¹ Three analysts determined alkalis with flame photometer.

The relative deviation of 3.5 percent for SiO₂ is reasonably good, but it does not suffice as a basis for rock classification and is definitely poorer than the chemical reproducibility, even if comparison is made with the interlaboratory chemical determinations shown in table 14. By making a quadruplicate analysis, the relative deviation could be reduced to a little less than 2 percent. There are a few geological applications of a spectrochemical method of silicon where a relatively coarse variation in the silicon content suffices as, for example, in the investigation of the geochemical association of Ge and Si in rocks.

For low concentrations of Si, as in a limestone, where precision of chemical analysis is probably lower than with igneous rocks, the spectrochemical method could successfully compete with the chemical procedure. Data on this aspect of the problem are not yet at hand.

When attempting to compare relative precision of chemical and spectrochemical analysis, it should be borne in mind that whereas personal error in a spectrochemical method is invariably slight, this cannot be said about chemical analysis. Therefore, although all spectrochemical determinations were made by only two analysts, the reproducibility would probably have been affected only a little had several other spectrochemists also made analyses.

In working with the alkali metals additional comparison of precision can be made using the flame photometer data already listed in table 16. Even though some of the determinations of the Geological Survey chemists were made with the flame photometer, the over-all precision is considerably less than that obtained from flame photometric data only.

THE ARITHMETIC MEAN AND THE CONSENSUS MEAN

Since the histograms of the chemical data show little approach to symmetrical form the task of selecting mean values for construction of spectrochemical working curves becomes a formidable one. If one assumes that the clustered values represent superior determinations and that the remaining values are inferior in quality, then a consensus mean—the mean of an arbitrarily selected cluster—should be used. If, on the other hand, one assumes that experimental error alone is responsible for the dispersion which is astonishingly large for certain constituents, then the arithmetic mean, computed from all the

TABLE 18.—Comparison of intralaboratory precision on selected constituents in granite (G-1) and diabase (W-1) samples

[Precision stated as relative deviations (C)]

	Chemical precision ¹	Percent concentration of constituent	Spectrochemical precision ²	Remarks
SiO ₂	0.3-0.6	50-70	3.5	Chemical analysis much superior.
Al ₂ O ₃	1-3	14-15	5-6	Chemical analysis superior.
Fe ^o	4-9	1-8	4-6	Spectrochemical analysis slightly superior.
MnO.....	15-30	.03-.2	9-13	Spectrochemical analysis much superior.
MgO.....	6-10	.4-7	6.5	Spectrochemical analysis superior in G-1.
CaO.....	.8-6.5	1-11	4-6	Chemical analysis superior in W-1.
Na ₂ O.....	$\left\{ \begin{array}{l} 3.6 \\ 1.5-3.0 \end{array} \right\}$	2-4	2.5	Spectrochemical analysis superior to chemical; about the same as flame photometer.
K ₂ O.....	$\left\{ \begin{array}{l} 3.4-7 \\ 1.0-2.5 \end{array} \right\}$.7-5	3-5	Spectrochemical analysis about the same as chemical; inferior to flame photometer.

¹ Except for Al₂O₃, precision in these chemical analyses increases directly (C becomes smaller) with increase in concentration of the constituent.

² Spectrochemical precision is independent of concentration of constituent.

³ Includes three flame photometer determinations noted in table 17.

⁴ Flame photometer only. (Massachusetts Institute of Technology values.)

TABLE 19.—Means of consensus groupings of constituents

Constituent	G-1				W-1			
	Mean based on fig. 1	Dispersion of consensus values (\pm mean)	Fraction of total analyses in consensus grouping	Mean based on figs. 3, 4	Dispersion of consensus values (\pm mean)	Fraction of total analyses in consensus grouping	Mean based on figs. 3, 4	
SiO ₂	72.45	0.05	1/2+	72.40	0.10	1/2+	52.35	
TiO ₂	.25	.05	1/2+	14.30	.05	1/2+	1.10	
Al ₂ O ₃	14.30	.10	1/2+	14.30	.25	1/2+	15.10	
FeO	1.85	.10	1/2+	1.90	.30	1/2+	1.50	
Fe ₂ O ₃	1.05	.05	1/2+	1.00	.05	1/2+	8.60	
MnO	.45	.05	1/2+	.03	.01	1/2+	6.00	
MgO	1.35	.05	1/2+	1.40	.05	1/2+	10.95	
CaO	3.35	.15	1/2+	3.40	.10	1/2+	2.10	
Na ₂ O	5.45	.05	1/2+	5.50	.05	1/2+	.65	
K ₂ O	.35	.05	1/2+	.40	.05	1/2+	.65	
H ₂ O	.10	.05	1/2+	.10	.05	1/2+	.13	
P ₂ O ₅						All		
Total	99.98		1/2+	100.15			99.82	
Total Iron as Fe ₂ O ₃	1.90	.10	1/2+		0.10	1/2+		

analyses, should be used. This mean has already been computed (table 14), and its relative position has been indicated on the histograms (fig. 1, 2).

Any consensus mean will be arbitrary and should therefore be selected carefully and used with caution. Two sets of consensus means taken independently and several weeks apart turned out, however, to be practically identical. One was taken from the histograms of part 2 and the other from those in this chapter. Table 19 shows these values, as well as arbitrary dispersion values, and the fraction of the total analyses occurring within the consensus grouping. The last-mentioned two columns were compiled from the histograms in part 2. If there is therefore any virtue in a consensus mean the selection shown in table 19 is probably as free from bias as any. The two sets of means are compared in table 20. The discrepancies are small, but should not be ignored on that account.

TABLE 20.—*Comparison of consensus and arithmetic means*

	G-1			W-1		
	Consensus mean greater by	Arithmetic Mean	Consensus mean less by	Consensus mean greater by	Arithmetic Mean	Consensus mean less by
SiO ₂	0.23	←72.22	0.01	0.20	←52.25	0.02
TiO ₂26→	.14		1.09→	.13
Al ₂ O ₃		14.44→	.09		15.23→	.40
Fe ₂ O ₃94→	.0		1.85→	.01
FeO.....	.0	1.00	.0	.21	←8.25	
MnO.....	.0	.03	.0		.19→	
MgO.....	.06	←.39	.13	←6.52		.0
CaO.....		1.42	.07	.0	10.95	
Na ₂ O.....	.09	←3.26	.05	←2.05		.06
K ₂ O.....		5.51→	.06	.71→		.07
H ₂ O.....	.0	.37	.0	.62→		
P ₂ O ₅0	.10	.0	←.13		

Three tests may now be applied toward a solution of the problem of whether the arithmetic or the consensus mean more nearly represents the theoretical composition of the two rocks. The first test involves comparison of the measured and calculated mode; the second is concerned with the problem of rejecting certain chemical determinations; the third involves a new set of analyses on a synthetic rock sample.

The first test makes use of the detailed modal investigation presented in part 5. These measured modes were made from thin sections prepared from the same slab of granite as was used for chemical analyses. It was thought that comparison of calculated modes—one based on arithmetic means, the other on consensus means—with these thin-section modes might give some indication as to the preferred set of means. The results of such calculations

are shown in table 21. Both calculated modes approximate the measured modes very closely, particularly for total feldspar. Both show somewhat higher quartz and lower mica than the thin section modes. The Al_2O_3 remainder is negligible in each case. The test is therefore inconclusive for present purposes, but nevertheless useful in showing that neither set of means is very far from the theoretical composition of the rock.

The calculated modes were made as follows:

- (1) All Fe_2O_3 was assigned to magnetite.
- (2) FeO not required for magnetite was assigned to biotite.
- (3) All MgO was assigned to biotite. The proportions of MgO and FeO thus available were about normal for biotite in granites.
- (4) Spectrochemical analysis of Al_2O_3 in this biotite gave 16 percent, corresponding to a biotite formula K_2O 5.6(Mg, Fe)O 1.4 Al_2O_3 5.6 SiO_2 2 H_2O .
- (5) Since the water available for muscovite after completion of the biotite calculation was far in excess of that required (ratio of muscovite to biotite, in measured mode, equals 2:5), the excess was disregarded and the muscovite calculation was based on the measured mode.

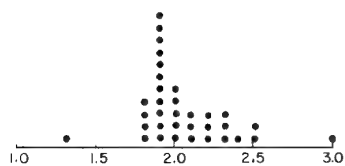
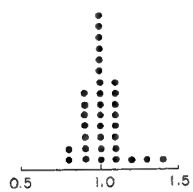
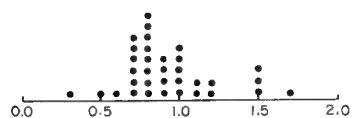
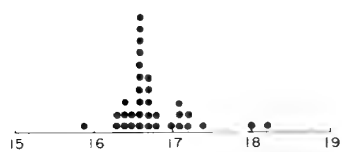
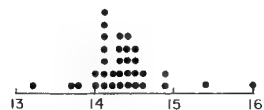
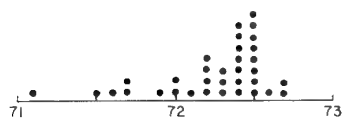
TABLE 21.—Comparison of measured and calculated modes of granite (G-1) sample

Minerals ¹	Measured modes (converted to weight percent)		Calculated modes	
	Mean of measurements by Chayes on 16 sections	Mean of M. I. T. meas- urements by 5 operators on 5 sections	Based on an arbitrary con- sensus mean for each con- stituent	Based on the computed mean for each constituent
Quartz	28.0	26.8	28.9	29.1
Total feldspar	65.9	66.7	65.8	66.3
Muscovite	1.4	1.4	1.1	1.0
Biotite	3.6	3.4	3.1	2.9
Magnetite	1.5	1.7	1.3	1.4
Total	100.4	100.0	100.2	100.7
Al_2O_3 remainder			0.9	0.7

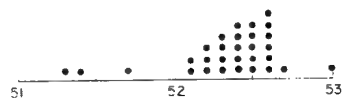
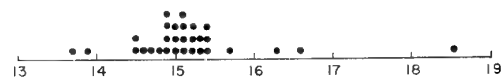
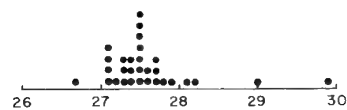
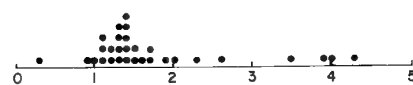
¹ Nonopaque accessories omitted.

- (6) K_2O not required for biotite and muscovite was assigned to orthoclase.
- (7) All Na_2O was assigned to albite.
- (8) All CaO was assigned to anorthite.
- (9) SiO_2 not required for the above calculations was assigned to quartz.

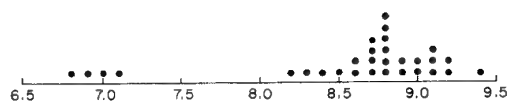
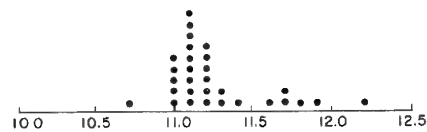
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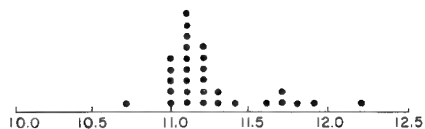
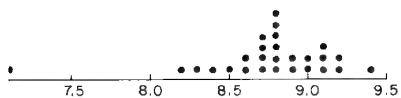
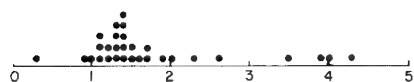
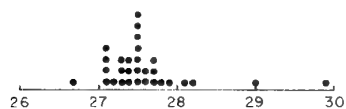
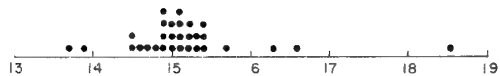
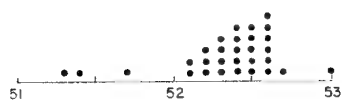
DIABASE

S O₂Al₂O₃R₂O₃Fe₂O₃

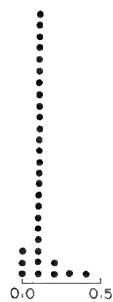
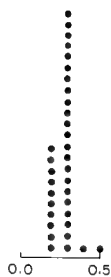
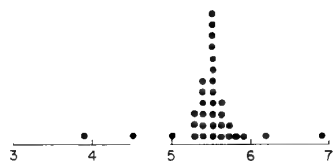
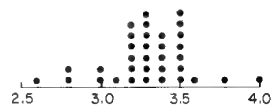
FeO

Total Fe
as
Fe₂O₃

DIABASE

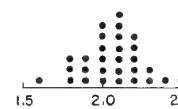


GRANITE

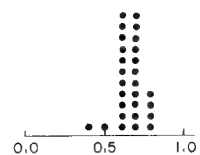


DIABASE

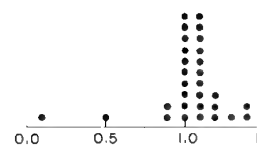
Na₂O



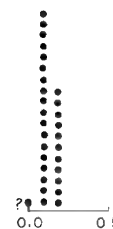
K₂O



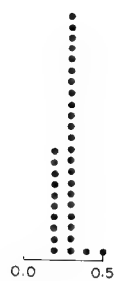
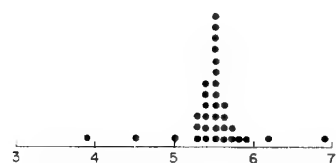
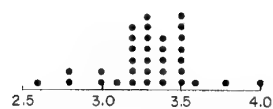
TiO₂



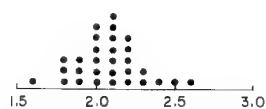
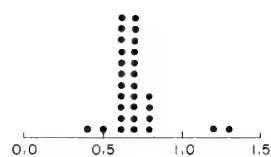
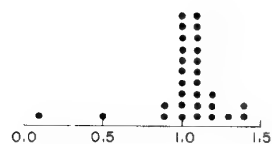
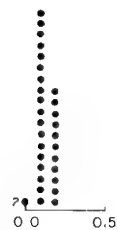
P₂O₅



GRANITE

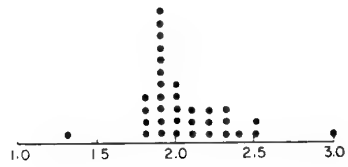
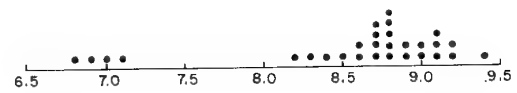


DIABASE

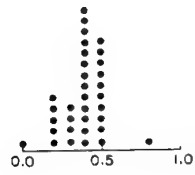
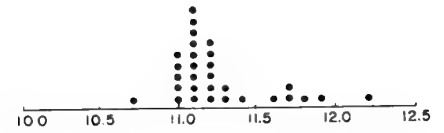
 Na_2O  K_2O  TiO_2  P_2O_5 



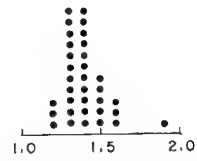
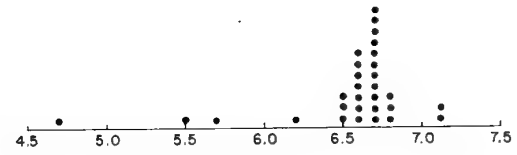
FeO



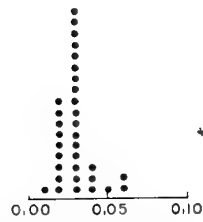
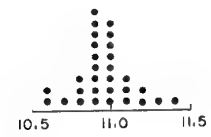
Total Fe
as
 Fe_2O_3



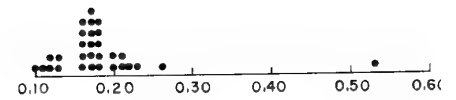
MgO



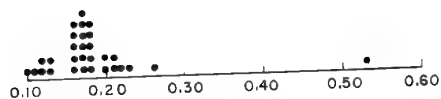
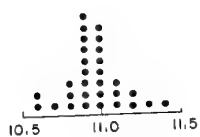
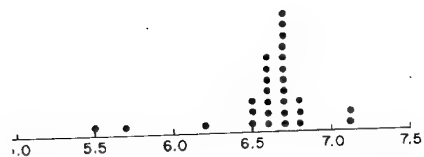
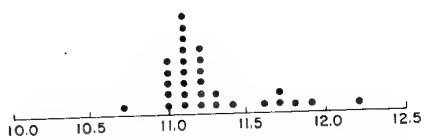
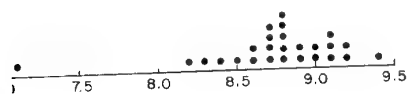
CaO



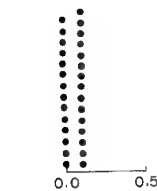
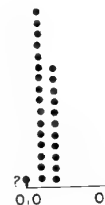
MnO



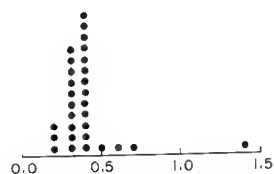
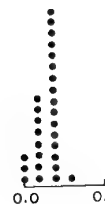
ANALYSES OF THE GRANITE AND THE DIABASE, AS



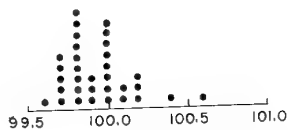
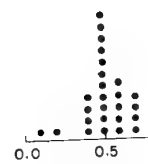
P₂O₅



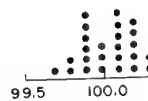
H₂O⁻



H₂O⁺



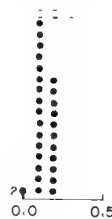
Summation



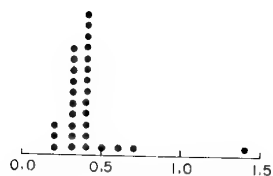
OF THE GRANITE AND THE DIABASE, AS REPORTED BY COLLABORATING ANALYSTS



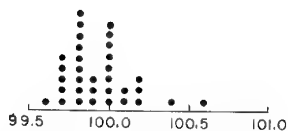
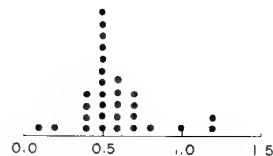
P_2O_5



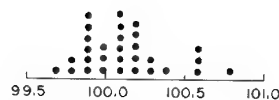
H_2O^-



H_2O^+



Summation



0.60

E, AS REPORTED BY COLLABORATING ANALYSTS

Orthoclase, albite, anorthite are reported as feldspar only, since the amount of K_2O in plagioclase, and Na_2O in orthoclase, was not determined.

The second test is somewhat more positive. The histograms (figs. 1, 2) show a number of determinations differing so markedly from the main group as to leave a reasonable doubt in one's mind that they could be attributed to normal experimental error. If a statistical device is used whereby measurements which differ from the mean by more than twice the standard deviation ($X - \bar{x} > 2s$) are discarded, it turns out that about 6 percent of them should be rejected altogether, and that an equal proportion are close to the discard threshold. Table 12 lists the rejected 6 percent. If the analyses are subjected to this test, less than half of the laboratories pass for all determinations; if one reject is permitted, less than two-thirds pass. The 34 rejected determinations are about equally divided between the two rocks and include every constituent except CaO in the diabase. The remaining histograms indicate for all except the TiO_2 in the diabase sample (W-1) a shift of the statistical mean in the direction of the consensus mean if the determinations listed in table 22 are omitted from the computation. This is shown by arrows in table 20, each directed toward the consensus-mean columns. Lest the reader suspect that in this test the "wish was father to the thought," it should be stated here that the consensus means were set up before there was any thought of applying this reject test. If therefore the premise is valid that the extremely low and extremely high determinations can be discarded, it would appear that a new statistical mean, closer to the consensus mean than now shown, should have preference.

The third test is essentially a new investigation, using as analytic material a synthetic rock of approximately the same composition as the natural granite or diabase already used. Since the composition of such a synthetic rock would be known within very definite and narrow limits, the work of a selected group of chemists could be closely controlled. If their determinations checked with the known composition of the synthetic standard, it might reasonably be assumed that their work on the two natural rock standards was equally significant and that their values should have preference over others. By this indirect approach a more reliable calibration for the spectrochemical working curves might be realized. This project, now under way, will be reported on at a later time.

TABLE 22.—*Compilation of rejected determinations in chemical analyses of standard rock samples*[Based on $X - \bar{x} > 2s$]

Number of rejects	Constituent	Rock sample		Number of laboratories
		G-1	W-1	
0				10
1	TiO ₂	x		5
	MnO	x	x	
	Na ₂ O		x	
	P ₂ O ₅	x		
2	Al ₂ O ₃	x		4
	Fe ₂ O ₃		xx	
	FeO	x	x	
	MnO	x		
	MgO	x		
3	P ₂ O ₅		x	2
	Al ₂ O ₃	x	x	
	Fe ₂ O ₃	x	x	
	K ₂ O	x	x	
5	H ₂ O+	x		1
	Al ₂ O ₃		x	
	MnO	x		
	MgO		x	
	CaO	x		
6	P ₂ O ₅	x		1
	SiO ₂	x	x	
	Fe ₂ O ₃		x	
	FeO	x	x	
8	K ₂ O	x	x	1
	TiO ₂		x	
	Fe ₂ O ₃		x	
	FeO		x	
	Na ₂ O	x		
	K ₂ O	x		
	H ₂ O+	x	x	
	P ₂ O ₅	x		

THE WORKING CURVES

The need for the foregoing discussion lies in its application to the construction of accurate working curves. In figs. 4-10, showing these working curves, the ordinate is a ratio of line intensities, that of the analysis line to the internal-standard line, which varies directly and linearly with the concentration of the analysis element. If standards of known concentration are available a working curve can be established for each constituent. These curves can then be used for analysis of unknowns.

In figs. 4-10 the degree of uncertainty is indicated by the form of each plotted point. For the diabase sample (W-1) and the granite sample (G-1) rectangles are employed in which the vertical side represents the error in the spectrochemical analysis; the horizontal side gives the corresponding error in the chemical analyses. The center of each rectangle is the plot of the mean values of the intensity ratio and of the chemical determination. The smaller the rectangle for a given constituent the more accurate is the working curve in the

neighborhood of that point. The relative degree of error in the two methods of analysis may be determined by the shapes of the rectangles. For standards appearing in the working curves other than diabase (W-1) and granite (G-1), the degree of uncertainty is unknown and the elliptical symbol used indicates only spectrochemical uncertainty.

The chemical values for G-1 and W-1 used in figures 4 to 10 are the computed ones (table 14)—figures 8-10 are based on computed means from flame-photometer data only. Although some evidence was assembled in the previous section favorable to the consensus mean, the dispersion of values about this mean (table 19) is greater in most cases than the computed errors of table 5. Until further chemical investigation with a synthetic standard is carried out, therefore, the degree of uncertainty in the standards is most logically shown by the computed error of the mean.

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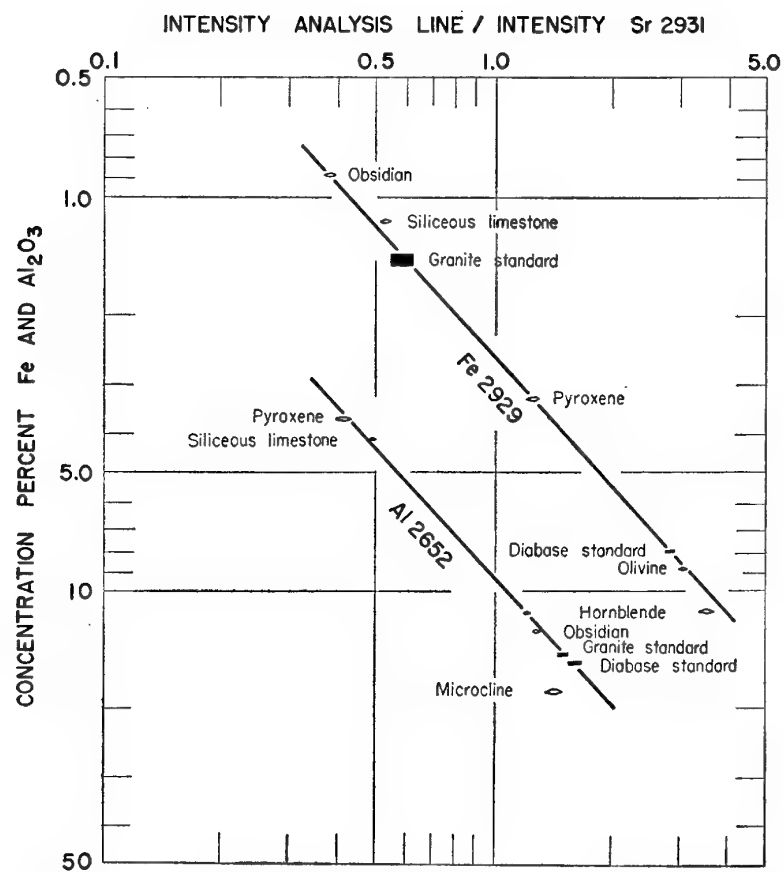


FIGURE 4.—Working curves for iron and aluminum. The aluminum point for microcline is unusually far off the working curve—perhaps because of a compositional effect. Obs, obsidian; W-1, standard diabase; Ls, limestone; G-1, standard granite; Py, pyroxene; Ol, olivine; Hb, hornblende; Mic, microcline. These are the standards referred to in table 1.

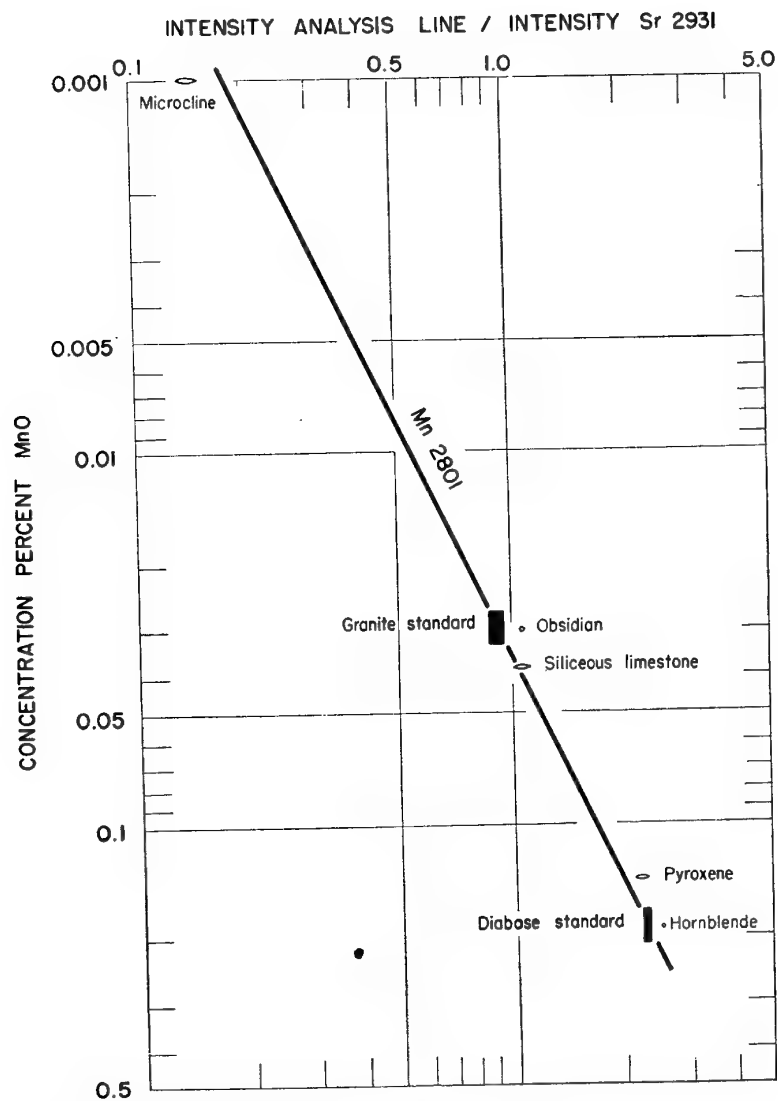


FIGURE 5.—Working curve for manganese. This curve is unusually flat. Abbreviations as in figure 4.

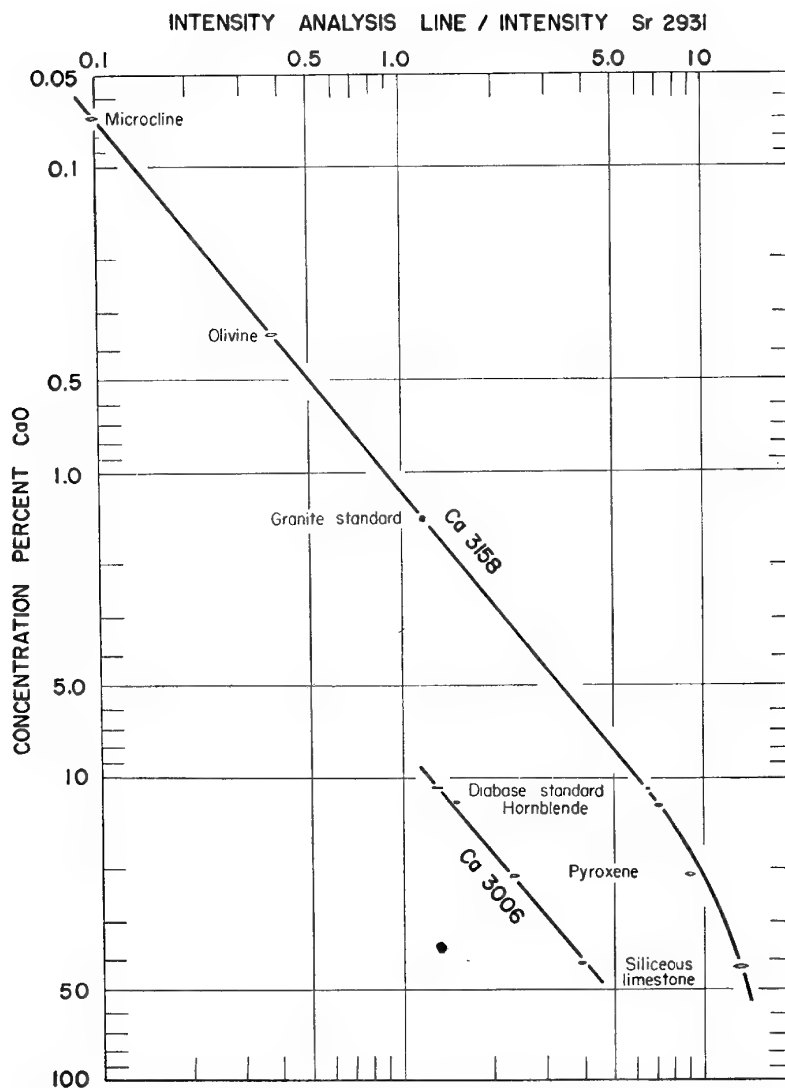


FIGURE 6.—Working curves for calcium. Because Ca 3158 begins to absorb above approximately 10 per cent CaO, Ca 3006 is employed at relatively high concentrations of calcium. Abbreviations as in figure 4.

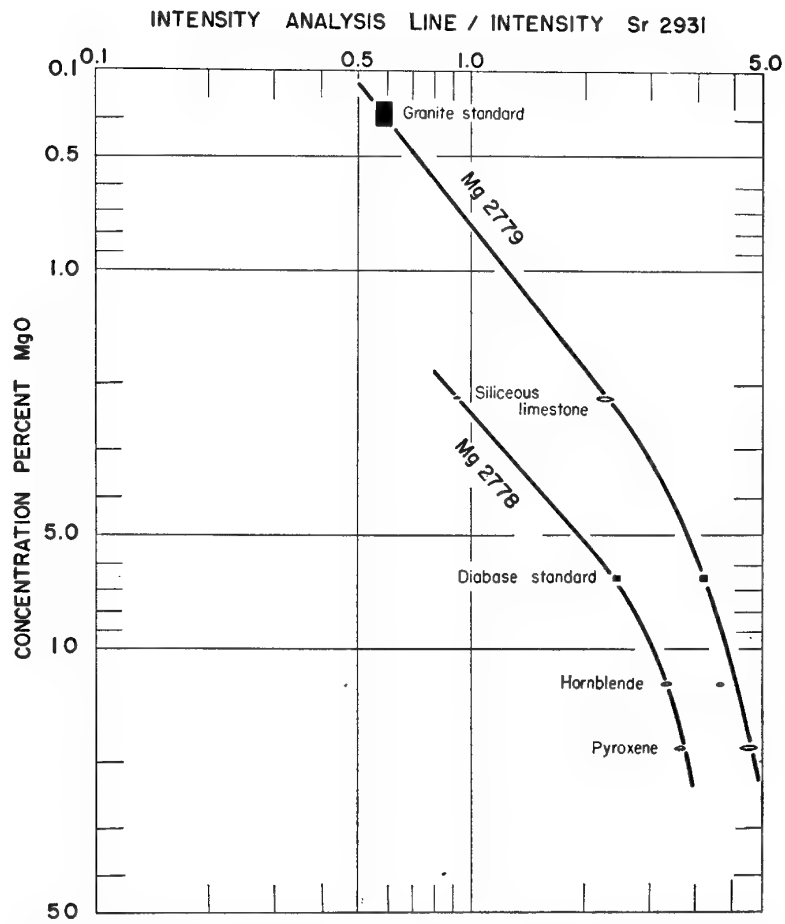


FIGURE 7.—Working curves for magnesium. Both exhibit the effect of self-absorption at relatively high concentrations of magnesium. Abbreviations as in figure 4.

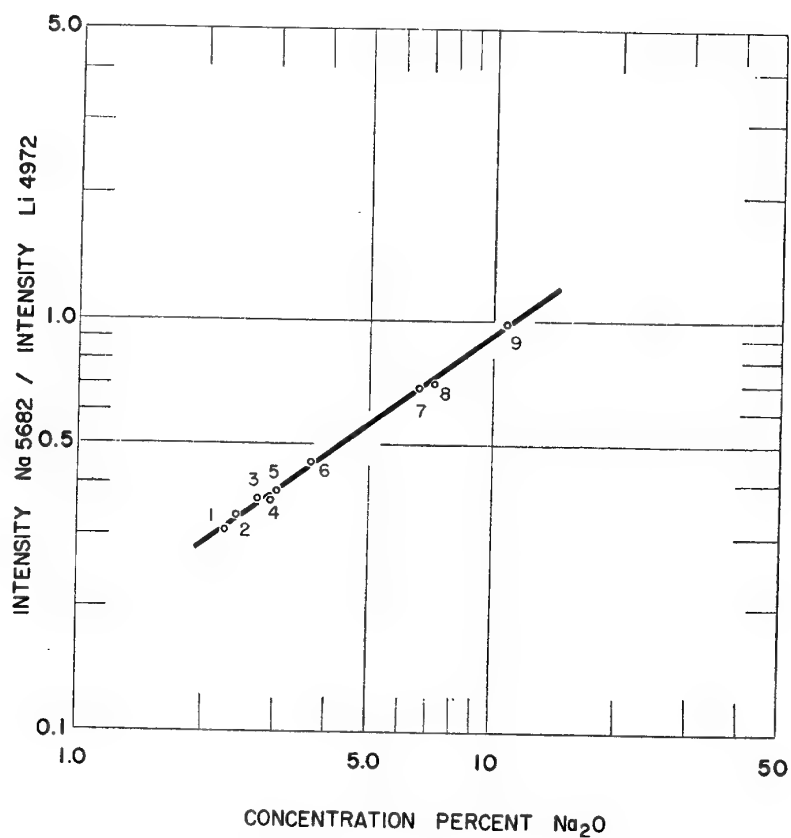


FIGURE 8.—Working curve for sodium. Plotted points closely spaced about the working curve.

1. W-1.
2. K feldspar (U. S. Bur. Standards, No. 70).
3. Two parts of W-1 and one part of G-1.
4. One part of W-1 and one part of G-1.
5. One part of G-1 and one part of K feldspar.
6. G-1.
7. One part of Na feldspar and one part of K feldspar.
8. One part of G-1 and one part of Na feldspar.
9. Na feldspar (U. S. Bur. Standards No. 99)

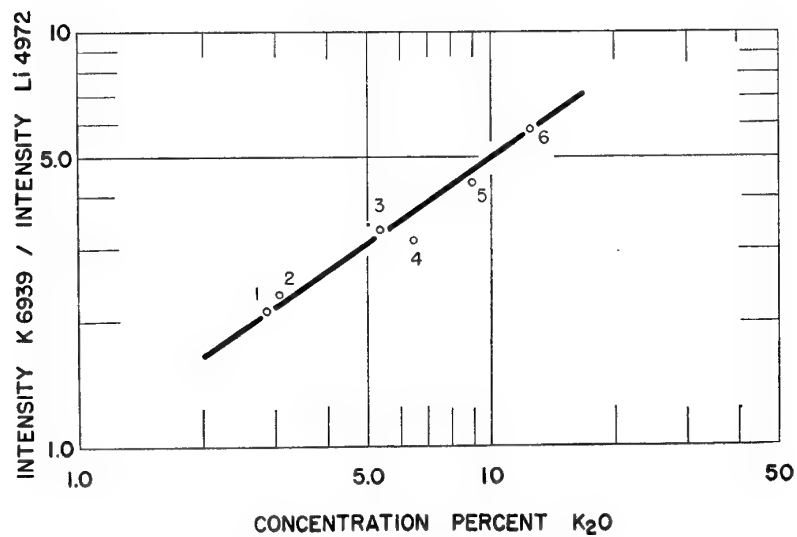


FIGURE 9.—Working curve for potassium (direct method). Restricted to concentrations above about 3 percent.

1. One part Na feldspar (U. S. Bur. Standards No. 99) and one part G-1.
2. One part W-1 and one part G-1.
3. G-1.
4. One part Na feldspar and one part K feldspar.
5. One part G-1 and one part K feldspar.
6. K feldspar (U. S. Bur. Standards No. 70).

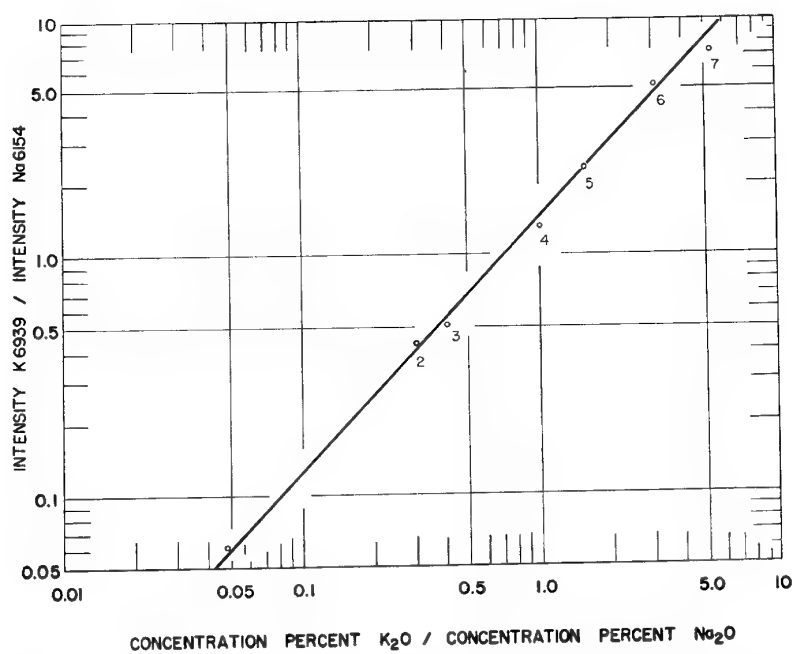


FIGURE 10.—Working curve for potassium (indirect method; sodium as variable internal standard). Applicable over a wide range of K/Na concentration ratios.

1. Na feldspar (U. S. Bur. Standards No. 99).
2. W-1.
3. One part Na feldspar and one part G-1.
4. One part Na feldspar and one part K feldspar.
5. G-1.
6. One part G-1 and one part K feldspar.
7. K feldspar (U. S. Bur. Standards No. 70).

A COOPERATIVE INVESTIGATION OF
PRECISION AND ACCURACY IN
CHEMICAL, SPECTROCHEMICAL, AND MODAL ANALYSIS OF
SILICATE ROCKS

**PART 4. SPECTROCHEMICAL ANALYSIS OF SOME OF THE
RARER ELEMENTS IN THE GRANITE AND DIABASE
SAMPLES**

By L. H. AHRENS⁴

INTRODUCTION

As sensitive and quantitative methods of analysis become available, increased attention is focussed on the abundance and distribution of the rarer elements in the earth's crust. Much of this information is based on spectrochemical methods of analysis, and in common rock types some 15 to 20 of the rarer elements may be determined by these methods. For a list of such elements see Ahrens (1950) and table 23 in this report. Several other elements may be determined provided that novel and lengthy procedures, some of which necessitate chemical pre-enrichment, are used. Here, however, we will be concerned only with those elements which may be determined by direct procedures.

There is little doubt that most published spectrochemical analyses are reasonably reliable insofar as they show the correct magnitude. The presence of a significant systematic error (see pt. 3) cannot, however, be overlooked. The presence of such an error makes it difficult to compare the analyses of a suite of minerals and rocks made by one analyst with the analyses of another suite made by another analyst. For example, the abundance of gallium in the igneous rocks from many areas of the earth's crust is about 0.0015 percent, according to spectrochemical analyses made by Goldschmidt and Peters (1931) and others. Van Tongeren (1938) also employed spectrochemical analysis for a study of the distribution of gallium and other elements in the East Indian Archipelago and obtained an abundance value for gallium three times that of Goldschmidt and Peters. Some geologists may conclude that the East Indian Archipelago as a whole is enriched in gallium. This is possible, but it seems unlikely when one takes into consideration the geochemical properties of gallium. Gallium is very uniformly distributed throughout the main mass of igneous rocks, and it would indeed be surprising for such an element to have enriched

⁴ Massachusetts Institute of Technology.

TABLE 23.—Comparison of spectrographic and chemical methods of analysis for rarer elements in the granite and diabase samples

Constituents	Granite standard ¹					Diabase standard				
	Spectrographic			Chemical		Spectrographic			Chemical	
	1	2	3	4 (Field test)	5 (Labo- ratory test)	1	2	3	4 (Field test)	5 (Labo- ratory test)
BaO	0.34	0.15	0.15	-----	-----	0.028	0.043	0.030	-----	-----
BeO	0	.00056	-----	-----	-----	0	.003	-----	-----	-----
B ₂ O ₃	-----	0	-----	-----	-----	-----	.0032	.0038	0.002	0.0052
CoO	0	.00038	0	0.0001	0.00038	.0044	.0032	.0038	0.002	0.0052
Cr ₂ O ₃0015	.0044	.0037	-----	-----	.018	.019	.016	-----	-----
CuO001	.0019	.00062	.001	.0025	.016	.011	.0055	.01	.016
Ga ₂ O ₃0027	.0024	.0026	-----	-----	.002	.0016	.0026	-----	-----
La ₂ O ₃050	.022	.015	-----	-----	.0038	0	0	-----	-----
Li ₂ O004	-----	.005	-----	-----	.002	-----	.002	-----	-----
MnO00082	.00082	-----	.002	-----	0	0	-----	.0007	-----
Nd ₂ O ₃	-----	-----	.0093	-----	-----	-----	-----	0	-----	-----
NiO0006	0	-----	.008	0	.006	.01	-----	.02	.010
PbO0027	.0024	.0025	.002	.0015	0	-----	.00078	.0006	.0006
Rb ₂ O065	-----	.06	-----	-----	.0016	-----	.007	-----	-----
Se ₂ O ₃	0	.00031	.0006	-----	-----	.0023	.0052	.0078	-----	-----
SiO ₂11	.014	.03	-----	-----	.05	.017	.030	-----	-----
V ₂ O ₅0025	.0038	.0027	-----	-----	.032	.032	.050	-----	-----
Y ₂ O ₃0038	.0032	.0030	-----	-----	0	-----	-----	-----	.011
ZnO	-----	-----	-----	-----	.0067	-----	-----	-----	-----	-----
ZrO ₂027	.026	.038	-----	-----	.0068	.013	.013	-----	-----
MnO	-----	.019	.031	-----	-----	-----	.18	.20	-----	-----

¹ Fluorine was determined spectrochemically (granite only) at Massachusetts Institute of Technology by R. H. Seraphim and L. H. Ahrens who obtained a value of 0.055 percent. For this analysis, use was made of standards prepared from analyzed phosphate rock (U. S. Bureau of Standards, No. 120) and diabase. Two analysts determined fluorine chemically; one gave a value of 0.04 percent and the other 0.09 percent.

² Rubidium analyses determined in three different ways.

³ A value of 0.0055 percent Se₂O₃ is given by A. Kvalheim.

by a factor of three over such a large area. The literature contains several statements about the enrichment, or impoverishment, of certain of the rarer elements in different areas; some of these statements are probably valid, but it seems that many merely reflect analytical variation.

In order to reduce systematic analytical error to a minimum, use may be made of the granite and diabase provisional standards. With each batch of specimens the analyst could analyze the standard diabase and granite samples, and in this way all results could be calibrated in terms of these two standards. Naturally, the standards themselves should be reliable; with this in mind, several spectrochemists are undertaking determinations of the rarer elements that they are able to handle, and from their determinations it should be possible to assign recommended values for each constituent.

In this paper (part 4) the available analytical data are presented, but recommended values for each constituent are not given because thus far only three complete sets of data are at hand. This paper is, therefore, much in the nature of a preliminary report, and a detailed account will appear later as a separate publication in which recom-

mended values will be given and where details of each spectrochemical method used will be provided.

At the time of writing, analytical data had been received from Dr. R. L. Mitchell, Macaulay Institute of Soils Research, Aberdeen, K. J. Murata, United States Geological Survey, Washington, D. C., and A. Kvalheim (scandium only, thus far) of Statens Raststoff Laboratorium, Oslo. The cooperation of these persons in spending much time in making complete analyses of each specimen is gratefully acknowledged. A third set of data, by Lorraine G. Gorfinkle and L. H. Ahrens, of the Cabot Spectrographic Laboratory, Department of Geology, Massachusetts Institute of Technology, also is available.

In addition to the spectrochemical analyses, some chemical determinations of certain of the constituents have been made by chemists at the United States Geological Survey, and very grateful acknowledgment is made for their cooperation. These analyses serve as useful checks for the spectrochemical determinations, and the chemical determinations are themselves checked by the spectrochemical determinations.

RESULTS AND DISCUSSION

Table 23 gives the spectrochemical determinations by R. L. Mitchell (column 1), K. J. Murata (column 2), and L. G. Gorfinkle and L. H. Ahrens (column 3), together with chemical determinations by field methods by Hubert W. Lakin, Hy Almond, Fred Ward, and Laura Reichen (column 4), and by laboratory methods by Harold Bloom (column 5).

No attempt is made in this chapter to draw any conclusions about spectrochemical precision and accuracy from the data given in table 23. When developing a method, a spectrochemist frequently makes replicate determinations from which he is able to compute the relative deviation—as a measure of precision. Rarely, however, is he able to evaluate the accuracy, unless the investigation involves a major constituent which may be analyzed chemically with a high degree of accuracy.

In general, the comments made in part 3 about the precision and accuracy of spectrochemical analysis apply also to the minor-constituent elements. Under ideal conditions the relative deviation may be 3 percent and values of 5 to 10 percent are not uncommon. However, as the concentration of an element approaches a level at which its most sensitive usable line begins to fade into background, precision deteriorates. In order to cover a relatively large number of elements in a relatively few operations, general spectrochemical

methods are often employed and these have been used in this investigation for the standard granite and diabase. The use of relatively general methods usually means a loss of precision, for although it is often possible to develop a precision method for a limited number of elements which have similar properties, this method is not really suited to the precise analysis of other elements. Usually a compromise between speed and precision is sought, because if many methods have to be employed to retain precision, the excessive time required would detract from the desirability of using a spectrochemical method. There are definite indications, however, that serious loss in precision need not be introduced by employing general methods and it is only a matter of time before really precise general methods will be available. One might compare the present state of affairs in the spectrochemical analysis of minerals and rocks with that of chemical analysis during the Berzelius era.

One encouraging feature about the results given in table 23 is that in general each analyst has reported on the same elements and no obvious errors are apparent. This may appear a silly statement, but "obvious" errors—mainly ones of reporting an element that is undoubtedly present at a concentration far below its detection limit—still appear in the literature. Factors such as type of instrument and technique employed do influence the number of elements an analyst is capable of handling, but in general each analyst should be able to analyze approximately the same number of elements. In the main, the agreement between the analysts is satisfactory: agreement on some constituents is very good, on some reasonable, and on a few, poor. Better agreement was not expected for several reasons. First, the reproducibility of the methods, expressed as relative deviation, varied from about 5 to 10 percent to 30 to 40 percent, and as the concentrations of some constituents border on concentrations at the limit of detection, still larger deviations would be expected for them; secondly, each analyst has employed an entirely different procedure; thirdly, the presence of significant systematic error is probable; and fourthly, some sampling error may have been introduced for the granite standard, particularly for Mo and Zr. The granite standard is a little coarser than is desirable, and for those methods which employ very small quantities of specimen—a couple of milligrams, as in cathode-layer excitation—a sampling error appears significant. The colorimetric determinations tally reasonably well with the spectrochemical determinations where the concentration of the element is sufficiently high to permit easy analysis for both spectrochemical and colorimetric methods; for example, cobalt in

diabase. In granite, where the concentration of cobalt is much lower, disagreement is more marked.

A fuller discussion on the results will be published later.

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A COOPERATIVE INVESTIGATION OF
PRECISION AND ACCURACY IN
CHEMICAL, SPECTROCHEMICAL, AND MODAL ANALYSIS OF
SILICATE ROCKS

PART 5. MODAL ANALYSES OF THE GRANITE AND
DIABASE TEST ROCKS

BY FELIX CHAYES⁵

MINERALS OF THE TEST ROCKS

As both test specimens are typical examples of extremely common rocks, an extended petrographic description is unnecessary. The diabase consists of augite and plagioclase (labradorite) with smaller amounts of quartz, potash feldspar, biotite, and opaque minerals. Although quartz is nowhere abundant it was noted in every thin section; no olivine was detected. Quartz is generally associated with potash feldspar in micropegmatitic intergrowth. Most, if not all, of the opaque material is oxide; sulfides were not found in a search of several thin sections under reflected light.

The granite contains quartz, microcline, plagioclase (oligoclase), small amounts of biotite and muscovite, almost 1 percent of opaque and about half of 1 percent of nonopaque accessories. As in the diabase, sulfides have not been detected. Nonopaque accessories include apatite, carbonate, fluorite, and tourmaline as well as occasional grains of sphene. The first three of these occur in every thin section, but apatite is easily the most abundant. Carbonate and muscovite are largely restricted to plagioclase, which is usually slightly clouded from alteration. As in almost all New England granites, biotite is sometimes replaced by chlorite; the replacement is rarely complete, and partially replaced flakes may occur in the same microscopic field with others that are entirely unaffected. A more complete description of the granite has been published elsewhere (Chayes, 1950).

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MODAL ANALYSES

Preparation of the test materials is described in part 1 of this report. It will be remembered that 8 small, evenly spaced blocks were broken out of the granite strip before the bulk of the sample was crushed. Thin sections were cut from both ends of each block so that there are in all 16 parallel thin sections spaced at alternate 4- and 6-inch intervals along the length of the strip. Thin sections were also prepared from 12 chips of the diabase, but the relation of these chips to each other in the original sample is not known. All slides were etched with HF and stained with sodium cobaltinitrite before covering. On each covered slide a continuous area of 500 mm.² was outlined, and in this area a point-counter analysis was run with a horizontal intercept distance of 0.3 mm. and an interval of 1 mm. between traverses.

Both rocks are fine-grained and well suited for modal analysis. Individual analyses are recorded in tables 24 and 25. Mean values and standard deviations are shown in table 26. No specific-gravity corrections have been used for the granite. For the diabase the following factors were applied to the volume percentages: Quartz, 2.66; potash feldspar, 2.56; plagioclase, 2.71; pyroxene, 3.30; biotite, 3.12; opaque accessories, 5.2; nonopaque accessories, 3.2. Application of these factors, of course, shifts mean values slightly for all constituents and considerably for plagioclase and pyroxene. Unless the factor is very large and applies to a major constituent, its effect on dispersion is negligible.

TABLE 24.—*Diabase modes converted to percent by weight*

Slide No.	Quartz	Potash feldspar	Plagio- clase	Pyroxene	Biotite	Accessories	
						Opaque	Non- opaque
1.....	0.8	2.3	46.8	45.9	1.4	2.6	0.1
2.....	1.7	2.7	45.7	45.0	1.4	3.1	.3
3.....	1.6	2.5	45.6	45.9	.9	3.5	.0
4.....	2.0	2.6	46.4	44.4	2.0	2.6	.1
5.....	1.8	3.7	43.6	44.9	1.8	4.0	.2
6.....	2.7	3.3	40.9	48.6	1.1	3.1	.2
7.....	2.7	3.4	44.6	44.0	2.0	3.1	.2
8.....	1.7	4.2	43.6	43.9	2.0	4.5	.1
9.....	1.3	1.8	48.3	43.0	2.7	2.8	.1
10.....	1.5	2.5	46.8	44.0	2.3	3.0	.0
11.....	1.9	3.6	44.2	44.2	1.9	3.8	.4
12.....	2.0	3.0	43.1	46.0	2.1	3.6	.1
Average.....	1.8	3.0	45.0	45.0	1.8	3.3	.2

TABLE 25.—*Granite modes, percent by volume*

Slide No.	Quartz	Potash feldspar	Plagioclase	Muscovite	Biotite	Accessories	
						Opaque	Non-opaque
13.....	27.8	35.6	30.2	1.7	2.7	1.1	0.9
14.....	25.5	35.4	33.0	1.7	3.1	.6	.7
15.....	29.6	34.4	30.6	.8	3.7	.5	.3
16.....	29.2	33.6	32.2	1.5	2.3	.9	.3
17.....	27.5	36.3	31.8	1.2	2.2	.6	.3
18.....	28.8	35.1	29.9	.9	3.8	.7	.8
19.....	28.4	33.6	30.9	1.9	3.5	1.4	.2
20.....	26.2	36.2	31.8	1.3	3.2	1.0	.3
21.....	27.8	34.6	31.7	1.5	3.0	1.1	.4
22.....	25.7	37.0	30.6	1.6	4.2	.8	.2
23.....	27.3	36.1	31.9	.7	3.2	.4	.5
24.....	29.1	36.3	29.1	1.4	2.7	1.2	.2
25.....	25.7	36.8	32.7	.9	3.4	.4	.1
26.....	27.9	32.0	34.2	1.2	3.8	.7	.2
27.....	25.6	37.1	32.4	.7	3.3	.5	.4
28.....	28.2	36.6	29.3	1.2	2.8	1.1	.6
Average.....	27.5	35.4	31.4	1.3	3.2	.8	.4

TABLE 26.—*Average modes for the test rocks*

Mineral	Diabase (12 sections)		Granite (16 sections)	
	Mean	Standard dev.	Mean	Standard dev.
Quartz.....	1.8	0.5	27.5	1.4
Potash feldspar.....	3.0	.7	35.4	1.4
Plagioclase.....	45.0	2.0	31.4	1.4
Pyroxene.....	45.0	1.5		
Biotite.....	1.8	.5	3.2	.6
Muscovite.....			1.3	.4
Opaque accessories.....	3.3	.6	.8	
Nonopaque accessories.....	.2		.4	
Average length of count.....		1345		1502

The results provide a useful check on the homogeneity of the samples prior to crushing. The analytical, or precision, error of point counting has been shown to be essentially binomial (Chayes, 1949), and it may be shown that the observed dispersions for major and minor minerals in the granite are not significantly larger than analytical error alone. That each of them is in fact a little larger than the corresponding theoretical estimate suggests some source of variation other than analytical error. But this source contributes so modestly, if at all, to the dispersion of each mineral that its presence could not be established without a much larger group of analyses. Scatter comparable to that observed might easily have resulted if a

single thin section had been analyzed 16 times instead of each of the 16 sections being analyzed once.⁶ For the diabase the situation is not quite the same. Pyroxene variation is suitably small, but plagioclase dispersion is a little large—as is the variation for both quartz and potash feldspar. This may be inherent in the sample but is more probably attributable to an unfortunate coincidence of inferior sections and inadequate staining. The slides were ground too thin and contained occasional holes. If these were sometimes not detected, they would be recorded as plagioclase or quartz. Similarly, incompletely stained potash feldspar might be tabulated sometimes as quartz and sometimes as plagioclase. Errors of either type would tend to enlarge the observed scatter for all three minerals, and this is probably what has happened. For reasons which will become apparent shortly, there seemed little need to repeat the analyses on a new set of slides.

COMPARISON OF MODES AND CHEMICAL ANALYSES

Chemical and spectrographic results are for the most part estimates of the same quantities and wherever this is true they may be directly compared with each other; in the absence of systematic bias the procedure which yields the smaller dispersion is preferable for a particular constituent. No such direct comparison of modes with either chemical or spectrographic analyses is possible. Yet *some* reasonable comparison of modes with analyses, particularly chemical, would be very useful to the petrographer, who is often compelled to rest content with thin sections when he would like to have analyses and almost as frequently tries to obtain from analyses information that could just as well be gotten from sections.

As neither rock is weathered and none of the major minerals is markedly abnormative, the CIPW norm provides a ready means of comparing modes with chemical analyses. Norms have been computed by mineralogists of the Trace Elements Section, Geochemistry and Petrology Branch, United States Geological Survey, and are shown with the analyses in tables 1 and 2. The average norms are shown in table 27, and agree quite well with the average modes. The

⁶ Since this was written a detailed test of the point counter has been undertaken by members of the geology department of the Massachusetts Institute of Technology. Five operators analyzed each of five of the slides whose analyses are shown in tables 24 and 25, each operator running the group in a different order. Agreement between mean values is admirable throughout and analytical error is not significantly larger than the theoretical precision error of the method except for biotite and muscovite. In this particular rock identification and tabulation conventions for the micas have proved difficult to standardize. Even for the micas, however, the excess of observed over expected analytical error, though clearly significant, is not large by standards usually applied to this type of work. The study was completed too late for inclusion here, and its results will therefore be published separately.

coincidence is not exact but the differences are readily explained.⁷

The largest discrepancy is between modal and normative pyroxene. Normative pyroxene contains neither alumina nor titania; all alumina, including that present in pyroxene, is calculated as feldspar, yielding an excess of normative over modal plagioclase. Titania is calculated as ilmenite, and quite appropriately there is a considerable excess of normative over modal opaque constituents. In the diabase the principal divergences between norm and mode may thus be reasonably attributed to simplifications in the calculation of pyroxene, simplifications inevitable if the actual composition of the pyroxene is unknown.

TABLE 27.—Comparison of norms and modes of test rocks

Mineral	Means		Standard deviations	
	Norm	Mode	Norm	Mode
Diabase (W-1)				
Quartz	4.1	1.8	1.7	0.5
Orthoclase	4.0	13.0	1.2	1.7
Plagioclase	47.6	45.0	2.3	2.0
Pyroxene	38.8	45.0	2.9	1.5
Opaque accessories	4.6	3.3	1.4	.6
Granite G-1				
Quartz	28.6	27.5	2.6	1.4
Orthoclase	32.5	35.4	2.8	1.4
Plagioclase	33.7	31.4	2.0	1.4
Opaque accessories	1.8	.8	.3	

¹ Potash feldspar—feldspar stained yellow on immersion in sodium cobaltinitrite solution after HF etch.

In the granite the principal discrepancies between norm and mode are in the feldspars and probably may be laid to the convention by which Na_2O present in potash feldspar is calculated as albite, increasing normative plagioclase at the expense of normative orthoclase. This is strongly indicated by the fact that the excess of normative over modal plagioclase (2.3 percent) is so nearly matched by the excess of potash feldspar over normative orthoclase (2.9 percent). Again, it is hard to see how such oversimplification can be avoided unless the composition of the potash feldspar is known.

It will be noted that each norm is richer in quartz than its corresponding mode. In the milling of such large quantities of rock there

⁷ The discussion of this section is intended to apply only to the subject matter of this paper. The problem is a very old one, however, and was admirably described in the original presentation of the CIPW system (A Quantitative Classification of Igneous Rocks, W. Cross, J. Iddings, L. Pirsson, and H. S. Washington, 1903, University of Chicago Press, pp. 112-113, and particularly pp. 146-153), in which all the explanations of discrepancies between mode and norm used here were first advanced.

is abundant opportunity for contamination by the grinding medium; flint pebbles were used in grinding the granite but the grinding medium used in preparation of the diabase is not known. Some of the excess of normative quartz in diabase may be due to the CIPW convention regarding titania, since in the calculation it not only takes up no silica itself but also ties up an equivalent amount of ferrous oxide which would otherwise be combined with silica.

Even in such simple rocks as these, however, exact coincidence of norm and mode is hardly to be anticipated. The important matter is that the agreement is quite fair as it stands, and this can mean only that by and large each major mineral is well represented by its normative analogue. With this in mind we may pass to a consideration of the columns headed "standard deviations" in table 24. Without exception the normative standard deviations are larger than those for the mode. Of course, widely discrepant chemical analyses are partly responsible for this curious situation, but the fault is not entirely theirs by any means; only by throwing away at least 25 percent of the analyses of each rock can normative dispersion be brought down to the same level as modal. Nor may the excessive variation of norms be attributed entirely, or even largely, to the conventions of calculation. The conventional *or* and *px* molecules vary less than would more complex normative parameters which attempted to represent the minerals more closely.

There is no escaping the fact that normative variation would be reduced far below the level of modal variation, if the interlaboratory reproducibility of chemical analysis justified results carried to hundredths of percents, as the standard statement encourages one to suppose. Actually the comparison of standard deviations in table 27 probably would face the other way even if agreement among the test analyses were ordinarily to a few tenths instead of to several tenths of a percent for certain key elements: alkalis and alumina in granite and alkaline earths, iron, and alumina in diabase.

For immediate purposes the modal results are important not because they look well alongside the norms, but because they provide direct assurance of the homogeneity of the test rocks. Judging by agreement between duplicates submitted by many analysts, the same assurance could have been obtained if any one of the analysts had been called on for replicate analyses. This procedure, however, would have been far more expensive, even supposing that an analyst could have been persuaded to run 12 or 16 entirely independent analyses of the same material.

From the viewpoint of the analytical chemist the results of the testing program afford no more than a description of the current state of affairs in rock analysis. They do not contain information

about biases in any of the determinations; except in a very crude fashion they do not gage the consistency of any analyst's work; and, unless one is prepared to regard agreement as a measure of accuracy, they afford no means of judging analyses or analytical procedures. The situation revealed by the test is probably more serious than many analysts realized, and it will certainly come as a shock to most geologists. But the only way chemists can take full advantage of the information is by obtaining more.

Although the comparison in table 27 is not very informative to the chemist, it is of immense value to petrographers. It should encourage us to place more reliance on adequately planned and carefully executed micrometric analysis for the accumulation of quantitative information about the mineralogical composition and variation of many common rocks. It should warn us against placing much assurance in comparisons of rocks or inferences about their variations based on collections of analyses culled from the literature. These are both matters of sufficient importance to warrant further discussion.

BEARING OF THE RESULTS ON PETROGRAPHIC PRACTICE

While theories about the origin and formation of rocks have multiplied and anastomosed at an alarming rate, the techniques of descriptive petrography have changed very little in the past half century. The continual interaction between hypothesis and observation which ought to characterize every healthy descriptive science is conspicuously lacking in petrography. This paralysis of the descriptive faculty, which finds us so often opposing theories to each other instead of testing them against observations, is no doubt the product of many and complex causes, some of which may be forever beyond our control. A large part of the difficulty, however, stems from the fact that resolution of many petrographic controversies requires abundant quantitative data, and we simply do not have the numbers. This unfortunate situation is a direct consequence of the hallowed tradition that the petrographer is willing to spend unlimited amounts of time in the examination, description, and interpretation of microtextures and structures which have been well-known since the days of Rosenbusch and Zirkel, but ordinarily feels no compunctions whatever about dumping on the shoulders of the chemist all responsibility for quantitative data about rock composition. Even the work of geologists who do their own analyses often reflects this sharp dichotomy between *qualitative* petrography and *quantitative* chemical analysis. By any standards, and certainly by standards the world usually applies to petrographic research, chemical analyses are expensive. Few petrographic projects can justify more than a handful of them, and this is simply not enough.

It is certainly fair to infer from table 27 that for the purpose of estimating the mineralogical composition of either test rock a single thin-section analysis contains about as much and about as reliable information as a single chemical analysis. Yet even for a comparative novice the thin-section analysis—by point counter—should not require more than a half hour if only 1,600 points are tallied, and for the experienced worker it is a matter of 15 minutes. For such exceedingly common rocks as the test samples and for many others as well, conscientious application of techniques now available would soon produce enough reliable quantitative information so that we could proceed to the long overdue task of separating the theoretical wheat from the chaff. Many rocks, of course, cannot be handled adequately by present techniques. Glasses and shales probably will always resist, but the point counter could easily be modified for use on large polished slabs to permit analysis of coarse-grained rocks. Where even this will not suffice, recourse to fragment analysis may be advisable. Special techniques will have to be developed for use on highly oriented rocks, of course, but in general there seems to be no reason why useful quantitative measurements should not be obtainable from any rock containing mineral grains of moderate size.

This is not to suggest that fewer rock analyses be made, for in fact we ought to have many more and far better chemical analyses. Even under optimum circumstances, however, the petrographer doing a detailed field study will rarely be able to afford more than a few analyses of any particular rock, and financial considerations usually oblige him to stop far short of this goal. Economy and speed are the real advantages of modal analysis, and together they offer the possibility of an enormous extension and amplification of our knowledge of rock variation. Provision of numerous reliable quantitative modes of each of the important petrographic units involved in his work ought to be regarded as a major responsibility by anyone working in eucrystalline rocks.

In another and equally important respect the test raises a problem for which there seems to be no solution. Except that all the chemical analyses listed in tables 1 and 2 are of the same two rock samples, their accumulation and tabulation parallels a very common petrographic practice. Toward the close of many petrographic reports there appears a section devoted to a comparison of the rocks in question with similar rocks exposed elsewhere and described, usually, by other workers. The qualitative aspects of such comparisons are generally admirable, and the stability of our descriptive techniques often makes it possible for us to take full advantage of work dating almost from the earliest development of the subject. The only quantitative comparison, however, is usually not of petrographic data at all; it is

in nearly every case a tabulation and discussion of chemical analyses culled from the literature.

Viewed in this light the scatter of the chemical results, whether as direct oxide percentages or as norms, must profoundly disturb every petrologist. The dispersion of oxide percentages is well shown in the histograms of figure 1, part 2. Normative variation is so extreme that in the absence of direct evidence to that effect there would be little reason to suppose all these analyses were of the same two rocks. Most of the diabase norms carry a few percent of quartz, but one shows 8.8 percent of that mineral and in another olivine is present to the extent of 5 percent. Normative plagioclase ranges from 43 to 56 percent in amount and from An_{46} to An_{73} in composition.

In the granite normative quartz varies all the way from 24 to 40 percent, a range wide enough to include almost all the granites in the world, yet many granites can easily be distinguished from each other on the basis of modal quartz alone. Most of the granite norms contain a little corundum, as they should since the rock contains a little muscovite. In 5 of the 33 analyses, however, the norms show more than a percent of corundum; in one of these there is 3 percent and in another 5 percent; in 5 other norms there is an actual deficiency of alumina so that some of the lime appears as diopside. In most granites—including the Westerly granite—the ratio of modal orthoclase to plagioclase is remarkably stable, and this ratio, or its normative analogue, is widely applied in rock classification. In the norms of the test analyses the ratio *or:pl* varies from 0.74 to 1.32. Normative plagioclase ranges in composition from An_5 to An_{24} .

Given the information that only two homogeneous samples are involved, we can make some attempt to separate the sheep from the goats and almost any reasonable ranking scheme brings the same analyses into question. But what could we do about these variations if we were told that the sample for each analysis was geographically distinct and the collection was of interest to us as a means of estimating the range of composition commonly exhibited by rocks of these two types?

The answer is dishearteningly clear; we could do absolutely nothing. A collection of individual analyses of each of a large number of rocks of the same type is bound to overestimate grossly the variability of the type, and collections of analyses of more than one rock type will necessarily underestimate the differences between types. Under these circumstances "transitions," "gradations," "gradual passages," etc., are demonstrated easily from almost any extended table, and we quickly come to feel that all divisions between rock types are arbitrary. It is easy to say that compilations of this sort exaggerate dispersion, but it is impossible to estimate the size of the exaggeration. Variation

among the test analyses is certainly very much larger than the internal variation of either rock and probably larger than differences between many related but reasonably distinct rock species. Providing rock types are defined independently of chemical composition, mean values computed from tables of analyses are probably quite good, though there is no way to find out just how good. But any approach which attempts to establish a difference between two or more rock types by means of comparisons which place much weight on individual analyses by different chemists is immediately suspect.

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A COOPERATIVE INVESTIGATION OF
PRECISION AND ACCURACY IN
CHEMICAL, SPECTROCHEMICAL, AND MODAL ANALYSIS OF
SILICATE ROCKS

PART 6. SUMMARY OF RESULTS

BY H. W. FAIRBAIRN [†]

It is the hope of the authors that readers of this bulletin will be both disturbed and encouraged by its contents. It is notorious that the twin themes of precision and accuracy have not been accorded their proper rank in many branches of quantitative geological work, partly through lack of data but in part also through disregard of the significance of these problems. In the fields of petrology and geochemistry at least, the present report is an emphatic reminder that evaluation of quantitative methods cannot be neglected.

To petrologists the discrepancies in many of the chemical analyses will be the most disturbing feature of this report, even if certain determinations are eliminated as grossly in error. The likelihood of occurrence of many of these discrepancies is of course commonplace to chemists and causes no surprise if the conditions of analysis are appreciated. Since, however, few petrologists are practicing chemists, the strong probability that analytical error is responsible for a large part of the total variation shown by a group of analyses is usually ignored. To make matters worse, the chemical data are in many cases obtained in such a way that it is impossible to separate the total variation into portions attributable to analytical error and true sampling variation. In the long run this lack of planning usually leads to gross overestimates of sampling variation. Furthermore, the common assumption that the same chemical precision can be realized for any constituent regardless of its relative concentration is thoroughly fallacious, so that interpretations of rock and mineral analyses which do not take this into account are of little value. Chemists know better, but as they are not usually interested in what petrologists do with their analyses, liaison is seldom established.

On the analytical side, the need for further interlaboratory collaboration by chemists is clearly indicated. With an adequate stock of

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homogeneous test material this could now be done. As outlined in part 3 an additional aim of the present investigation is to obtain, by means of a synthetic rock standard, better agreement on the two original standards. If this is possible, chemists will in the future have a more reliable base for checking their work. The results of the present investigation may serve as a guide in evaluating previously published work; they indicate that analyses by the same chemist, or by different chemists from the same laboratory—assuming fixed operating conditions—can probably be used for comparative work in petrology; on the other hand, comparisons of analyses made in different laboratories had best be used with extreme caution. As Chayes points out (pt. 5) ranges reported in the granite and diabase standards are greater than compositional limits for related but distinctly different rock types. Discrepancies in determination of alkali metals are particularly critical in this regard, since to a large extent feldspar composition controls rock classification. It would appear that more widespread use of flame photometric and spectrochemical methods would improve the quality of alkali metal determinations. (See pt. 3.)

Average analyses of rock types might profit by reappraisal of certain details. As far as silica (SiO_2) is concerned the variation from one rock to another related one is large enough that chemical discrepancies are negligible. This is not true for many of the other constituents, particularly if their concentration is low. The retention of two figures beyond the decimal point, except for very minor constituents, becomes ridiculous for most petrologic purposes. The chemist is justified in presenting his results in this way since addition to 100 percent is a test of his work. Petrologists, however, should ruthlessly discard unnecessary detail beyond the decimal point.

Compared with chemical procedures, spectrochemical methods are in their infancy. Nevertheless, present evidence shows, for spectrochemical determination of the major elements, precision comparable with that of chemical methods (pt. 3, table 18) and they have as added advantages the saving of time and money, the use of a small sample, a permanent record of the spectrum. Although few spectrographic laboratories are at present in a position to do work of this kind, there is every reason to believe that their numbers will grow. The chemical laboratory will never be displaced, since a chemist will always be required to determine water (H_2O) and iron oxide (FeO) and, in ordinary silicate rocks, silica (SiO_2), because of its high concentration. At present, also, phosphorus pentoxide (P_2O_5) remains within the province of the chemist. It would appear then that a happy marriage of chemical and spectrochemical procedures would do much for the petrologist and geochemist. Both techniques require skilled

analysts and adequate interlaboratory standardization. From now on it is not too much to expect that these requirements will be met.

Passing down the scale to concentrations of elements beyond the scope of chemical procedures, it is obvious that for the spectrochemist much interlaboratory calibration remains to be done. Methods themselves are inadequately standardized. As in any form of analysis, procedures giving high precision and accuracy are time-consuming. However, as is pointed out in part 4, lower orders of precision and accuracy are often adequate and can be obtained in much shorter time. Published abundance values for minor elements in the earth's crust need critical review, since they are based on work in a few laboratories only, with no interlaboratory standardization whatever. As already noted in part 3 this standardization, using the granite and diabase provisional standards, should not be difficult to achieve.

Precision in modal analysis of thin sections has now been carried to a much higher level than heretofore and the method emerges as a more potent weapon for petrographers than was formerly thought possible. Here, as in chemical and spectrochemical work, interlaboratory checking is advisable, and in fact it is now in progress. Modal analysis is a purely petrographic tool, developed by petrographers for petrographers, and deserves more prominence in their work than it has received. The method involves neither costly apparatus nor great expenditure of time and gives results obtainable in no other practicable way.

It is the hope of the authors that critical evaluation of analytical data will in future be the rule rather than the exception. Such evaluation should have been commonplace a generation ago. It is our hope that the work described in these pages will initiate similar, more extensive, and better designed studies of the accuracy and precision of analytical methods used by petrologists, geochemists, and mineralogists.

